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OUTLINES OF CHEMISTRY,

FOR

THE USE OF STUDENTS.

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OUTLINES OF CHEMISTRY,

For the Use of Students.

BY

WILLIAM GREGORY, M.D.,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

WITH ENGRAVINGS ON WOOD.

SECOND EDITION, REVISED AND ENLARGED.

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PREFACE.

The present work is designed exclusively for the use of students attending Lectures on Chemistry, and is more particularly adapted as a Text-book for my own Lectures. It has no pretensions to any more important character; and is so far from being intended as a substitute for any of the larger elementary works, that its chief value, if it possess any, will be, that it serves as an introduction to those works.

Every teacher of Chemistry must have felt the want of a compact text-book, the price of which might place it within the reach of every student; and it is the long-felt sense of this want which has led me to compile these outlines. The importance, to beginners, of having some such guide, and some such help to the memory, cannot, I believe, be overestimated.

Some apology, or explanation at least, may seem to be required for the omission of certain subjects, usually treated of in elementary works on Chemistry. I allude to the subjects of Heat, Light, Electricity, and Magnetism: in short, to the Imponderables. It is not without ample consideration that I have taken this step.

For nearly ten years past, I have been in the habit, in my lectures, of treating these subjects very briefly, partly because, in my opinion, they belong almost entirely to the province of Physics: but also, and chiefly, because the enormously increased extent and importance of Chemistry, especially of Organic Chemistry, rendered every moment of time, in a course of lectures which at best could be but imperfect, precious in the highest degree.

Since I had the honour to be appointed to the Chair of Medicine and Chemistry in the University and King's College, Aberdeen, in 1839, I have altogether discontinued the teaching of the above-mentioned subjects *as regular sections of the course;* and have only taught them incidentally, that is, where they naturally come into very close connection with Chemistry; and by this means I have been enabled to devote about three months, out of five and a half, to Organic Chemistry, a branch of the subject of the highest importance to medical students, and, as is well known, of daily increasing interest and value, from its applications to physiology and to the useful arts. I am inclined to believe that, if, by the omission of the Imponderables as a regular part of the course, anything has been lost, the comparatively full, although yet too brief, development of Organic Chemistry has furnished more than sufficient compensation.

But, in truth, the Imponderables are now very generally, as they undoubtedly ought to be, taught as a part of Physics by the lecturers on Natural Philosophy, so that the teacher of Chemistry is not absolutely required to do more than to explain their most important bearings on Chemistry.

It is probably on account of such considerations that the opinion has long been gaining ground among teachers of Chemistry, that it would be desirable to confine their attention more particularly to matters essentially chemical, than to those branches of Physics which are in some measure related to Chemistry. But although this opinion is very general, the habit of teaching these branches of Physics as part of our courses of Chemistry has still continued to prevail; and, consequently, the appearance of a chemical text-book without them will appear to many a novelty.

I wish it to be clearly understood, that, in omitting these subjects, I am not actuated by any doubts as to their great importance and value to the chemist. It is necessary that the chemist should be well acquainted with them, at least in so far as they bear on his own science; but it is impossible for the teacher of Chemistry, who gives a fair view of its present state, to undertake, in addition, the teaching of so great a part of Physics. The student of Chemistry must obtain that knowledge elsewhere, just as he does his knowledge of arithmetic, mathematics, or mechanics, all of which are highly useful to him, but which the chemist is not expected to teach.

The present work, therefore, is to be viewed as giving a brief sketch of the Chemistry of *ponderable substances only;* and with the experience of several years in teaching this Chemistry, with only occasional and incidental references to the Imponderables, I venture to testify that this method of instruction in Chemistry has many advantages over the old one; in particular, that this alone enables the teacher to do justice to Organic Chemistry.

The reader will perceive that while I have given both the rival theories of the constitution of Acids and Salts, I have indicated a decided preference for the new one, that, namely, which considers all *hydrated oxygen acids* as really *hydrogen acids,* and thus unites all acids into one series, while salts are viewed as compounds in which the hydrogen of acids is replaced, wholly or partially, by its equivalent of metals.

This theory, along with the usual view of acids and salts, will be found minutely illustrated in the sections which treat of the acids formed by sulphur and oxygen, of the phosphoric acids, of salts generally, and of the phosphates in particular.

In close connection with the theory of acids and salts, stands the doctrine of polybasic acids, which in the present state of our knowledge appears to be so well founded, that we must admit it, and so simple that it materially facilitates the teaching of what would otherwise be most complicated and difficult. This doctrine I have adopted and fully illustrated under the heads of Phosphoric Acid and the Phosphates. But while adopting, on these points, the views held by Professor Liebig, I agree with him in considering them not as permanently established truth, but only as best agreeing with the facts known to us, and therefore the best theoretical doctrines within our reach, although likely, nay, certain, in process of time, to be modified or even replaced by better, the natural result of improved knowledge. In the mean time they serve an important purpose ; that, namely, of enabling us to systematise or classify our actual knowledge, and thus to obtain fresh starting-points for new researches.

There is one more feature of this work to which I would direct attention. In describing chemical processes, or chemical changes, I have, as a general rule, added to the verbal description a representation of the reaction in the form of an equation, exactly as I am in the habit of doing in my lectures. This method I have found most advantageous, and it gives me great satisfaction to find that Professor Gmelin, in the new edition of his " Handbuch," has followed exactly the same plan. The use of such equations enables us to place the most complex reactions in the clearest point of view ; and they also furnish data for all the calculations which are so often required in the laboratory.*

The brevity with which Inorganic Chemistry has here been treated has enabled me, in the second Part, without adding to the intended size or price of the work, to devote to Organic Chemistry a space proportionate to its importance, and to the share of time allotted to it in my lectures.

In preparing the present edition of the Organic Part, I have been compelled, although but a short time has passed since the first edition appeared, in consequence of the rapid progress of the science, to make considerable changes in several important sections ; of which I may specify those on the Organic Bases, on the Albuminous substances, and the Nitrogenised colouring matters. In other sections, it has been necessary to make large additions, as has been done, for example, in treating of the Volatile oily acids, of the derivatives of Benzoyle, of the derivatives of Uric acid, of the various kinds of fermentation, of the artificial organic bases, of the juice of flesh and its constituents, and in several other instances; the added matter extending to one-sixth of the work.

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* Those readers of this work, among the students of the University of Edinburgh, who may wish to perform for themselves the experiments and processes described, will find the necessary apparatus and materials, and reasonable charges, in the establishment of Messrs. KEMP & Co., opposite the College.

No change has been made in the plan of the work, and I trust that the favourable reception which it has met with may be considered as proving that it has, to a considerable extent, fulfilled the object which I had in view, namely, to provide the student with a compendious and portable manual of the actual state of the science.

WILLIAM GREGORY.

University of Edinburgh,
11*th Nov.*, 1847.

TO THE READER.

In the interval between the printing of the earlier sheets of Part I. and the later sheets of Part II., Chemists have pretty generally agreed to double the equivalents of Phosphorus, Arsenic, and Antimony. The reader is requested to make this alteration in the equivalents, and also to substitute, in the formulæ, the symbols P, As and Sb, for P_2, As_2, and Sb_2, wherever the latter occur, as, for example, in the case of phosphoric acid, $P_2 O_5$, which is now PO_5.

W. G.

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OUTLINES OF CHEMISTRY.

INTRODUCTORY.

The world in which we live is formed, in its different parts, of a number of distinct kinds of matter, amounting, according to the present state of our knowledge, to about 55. These are called elements, elementary bodies, or simple substances.

The forms of matter with which we are most familiar, however, are not elementary. If we examine the matter of which a rock, a tree, an animal, the atmosphere, or the ocean is respectively composed, we shall find that all those objects may be proved to contain two or more distinct kinds of matter; that is, two or more elements. Where this is the case, we call the substance a compound body.

A compound, therefore, may be resolved into its elements; whereas an element, or simple substance, cannot be made, by any means yet known to us, to yield more than one kind of matter. Brass, which is compound, may be resolved into copper and zinc; but from copper or zinc we can obtain only copper or zinc. Vermilion may be shown to contain sulphur and mercury; but sulphur can only be made to yield sulphur, and mercury, mercury.

But when we call any substance elementary, or simple, we do not mean that it is certainly or essentially so; we only say that hitherto, in our hands, and exposed to all the various agencies which we can bring to bear on it, it has yielded only one kind of matter, or element, and no more. In the early part of the present century, the alkalies and earths were believed to be elementary bodies, because only one kind of matter had ever been obtained from them; but the new power of galvanism enabled Davy to discover that all these bodies were compound. It is far from being improbable that, in the progress of discovery, several, perhaps many, of the 55 elements which we are now compelled to admit, may, in like manner, prove to be really compound bodies.

Till then, however, we must be content to class together, as elements, all those bodies which have not yet been resolved into other kinds of matter; and of these undecomposed bodies, or elements, all material objects are constituted. Here follows the list of the elementary bodies at present admitted, with the abbreviation, or symbol, which is used for each element placed after the name:—

ELEMENTS.

Oxygen	O
Hydrogen	H
Nitrogen	N
Sulphur	S
Phosphorus	P
Carbon	C
Chlorine	Cl
Bromine	Br
Iodine	I
Fluorine	F
Boron	B
Silicon	Si
———	
Selenium	Se
———	
Potassium (Kalium)	K
Sodium (Natrium)	Na
Lithium	L
Barium	Ba
Strontium	Sr
Calcium	Ca
Magnesium	Mg
Aluminum	Al
Glucinum	G
Yttrium	Y
Zirconium	Z
Thorium	Th
Cerium	Ce
Lantanium	La
Didymium ?	
Erbium ?	
Terbium?	
Manganese	Mn
Iron (Ferrum)	Fe
Cobalt	Co
Nickel	Ni
Zinc	Zn
Cadmium	Cd
Lead (Plumbum)	Pb
Tin (Stannum)	Sn
Bismuth	Bi
Copper (Cuprum)	Cu
Uranium	U
Mercury (Hydrargyrum)	Hg
Silver (Argentum)	Ag
Palladium	Pd
Rhodium	R
Ruthenium ?	
Iridium	Ir
Platinum	Pt
Gold (Aurum)	Au
Osmium	Os
Titanium	Ti
Columbium (Tantalum)	Ta
Pelopium ?	
Niobium ?	
Tellurium	Te
Tungsten (Wolfram)	W
Molybdenum	Mo
Vanadium	V
Chromium	Cr
Antimony (Stibium)	Sb
Arsenic	As

(The symbols or abbreviations are in every case taken from the Latin names of the elements, so as to be universally understood. Should the existence of the new metals, discovered by Mosander, viz. Didymium, Erbium, and Terbium, as well as of those announced by Rose, viz. Pelopium and Niobium ; and of the metal, Ruthenium, found by Klaus in the ore of Platinum, be established, the number of the elements will be 61.)

Of the above list of elements, about 14 constitute the great mass of our earth and of its atmosphere. The remainder occur only in small quantity, comparatively ; while nearly a third of the whole number is so rare, as not to admit of any useful application.

By their external aspect, the elements may be divided into two classes ; and these classes are also found to possess other distinctive characters. Thus the twelve first in the list, which are called non-metallic bodies, or metalloids, are easily distinguished from all those after potassium, inclusive, which are metals. The latter possess that peculiar brightness and opacity of surface which is called the metallic lustre, of which the former are destitute. Again, the metals are all found to be excellent conductors of heat and electricity, while the metalloids conduct these influences very badly, with the exception of charcoal, which, when in certain states, conducts electricity almost like a metal.

Selenium has the metallic lustre, and is by some considered a metal ; but it is a non-conductor of heat and electricity, and in all its chemical relations and analogies belongs to the non-metallic bodies.

This division of the elements is of great use in facilitating the study of chemistry.

The elements are capable of combining together, metalloids with metalloids, metals with metals, and metalloids with metals.

When two elements unite together, they give rise to a new substance, a compound of the two ; and, generally speaking, the compound has properties entirely distinct from those of its elements. Thus, sulphur and mercury, a yellow earthy solid and a white fluid metal, unite, and give rise to a fine red powder, which is vermilion. It is not possible, by the eye, to distinguish two kinds of matter in the vermilion, any more than in its elements, so completely have the properties of those elements disappeared. But, by chemical means, we can prove that vermilion contains both mercury and sulphur. These elements are said to be combined, so as to produce vermilion, which is said to be a compound, or to be composed of them. In such a case, the combined elements can no longer be separated mechanically from each other. They are held together by a force which is called chemical attraction, or *affinity*, the real nature of which we do not know. It resembles cohesion, since it holds together the particles of matter: but while cohesion is only exerted between particles of the same nature, as, for example, between those of sulphur, or between those of vermilion, affinity is only exerted between particles of different kinds of matter, for example, between the particles of sulphur and of mercury.

By affinity, then, we understand simply that force, whatever may be its nature, by which the particles of one elementary body are made to unite with those of another. When once united, the particles of the compound obey the laws of cohesion exactly as if they were simple particles.

It is the object of chemistry to investigate the properties of the elements, the laws which regulate their mutual actions, and the nature and properties of the compounds which arise from their union.

Before describing the individual elements, it is necessary to explain to the reader certain terms and phrases of very frequent occurrence, as well as to mention the general laws which regulate chemical combination.

Combination occurs when two or more bodies unite together: *decomposition* takes place when bodies, previously united, are made to separate from each other.

When oxygen enters into combination with any other element, the compound is called an oxide; the compound of chlorine with any other element is called a chloride: and with bromine, iodine, and fluorine, we have, in the same way, bromides, iodides, and fluorides. The compounds of sulphur, phosphorus, carbon, selenium, &c., with metals, are called sulphurets, phosphurets, carburets, seleniurets, &c.

When a compound body possesses a sour taste, reddens vegetable blue colours, and neutralises alkalies, it is called an acid. If composed of oxygen united to a metalloid, such as carbon, or a metal, such as chromium, the acid is simply named from the metalloid or metal, as carbonic acid, chromic acid. But if the acid contains hydrogen united to a metalloid, the word "hydro" is prefixed; as hydro-chloric acid (hydrogen and chlorine), hydro-sulphuric acid (hydrogen and sulphur), &c.

Where the same element forms with oxygen several acids, they are distinguished by their terminations, as sulphuric acid, sulphurous acid; the acid in *ic* always containing most oxygen: but where new acids of intermediate composition are discovered, it is necessary to use the prefix "hypo,"—as hypo-sulphurous acid, hypo-sulphuric acid, meaning acids containing less oxygen than sulphurous or sulphuric acids respectively;

or "hyper," as hyper-chloric acid, meaning an acid containing more oxygen than chloric acid.

When a compound body has an acrid, urinous taste, restores to blue the colour reddened by an acid, and, above all, if it possess the property of neutralising acids, or causing their acid properties to disappear, it is called an alkali, or more generally a base, or a basic substance.

We have seen that oxygen is an element of many acids; it is also an element in most bases. Almost all the metals are capable of forming one base, several form more than one base, with oxygen. These bases are usually called oxides of the metal; and where there are two, that which contains least oxygen is usually called protoxide, and that which contains most oxygen, peroxide; as the protoxide and peroxide of iron, &c.

Acids and bases unite together, and the characteristic properties of both disappear. They are said mutually to neutralise each other, and the resulting compound is called a salt. If neither the acid nor base be in excess, the salt is a neutral salt; if the acid predominate, it is called an acid salt, or a super-salt, and if the base prevail, it is called a basic salt, or a sub-salt. The salt is named from both the ingredients. Thus, when sulphuric acid neutralises soda, the resulting salt is called the sulphate of soda; when phosporic acid unites with lime, the acid being in excess, the salt is called acid phosphate of lime, or superphosphate of lime; and when nitric acid unites with oxide of mercury, the latter being in excess, the compound is called basic nitrate of mercury, or subnitrate of mercury.

Besides acids and bases, there is a third kind of oxides, namely, such as have neither acid nor basic properties. They are called indifferent oxides, and sometimes superoxides; as, for example, peroxide, properly superoxide of manganese.

The term "radical" is applied to any body which, by uniting with an element, can give rise to an acid or a base. Most of the elements play the part of radicals: but we have, besides, compound radicals, containing two elements, like cyanogen, or even three or more elements, like benzoyle or kakodyle. The compound radicals unite with elements, just as if they were themselves elementary. Thus, cyanogen unites with hydrogen to form an acid, and kakodyle unites with oxygen to form a base.

COMBINATION.

The force of chemical attraction, or affinity, is unequal in the case of different substances. Thus, the affinity between potassium and oxygen is more powerful than that between gold and oxygen.

The capacity of one body to unite with another is mainly effected by two circumstances; namely, the state or form of the substances in question, whether solid, liquid, or gaseous, and the temperature at which they are brought together.

Cohesion tends to keep the particles of bodies in close proximity, while the tendency of heat is to separate them from each other. When cohesion predominates over the repulsion due to heat, the body is solid: when cohesion and repulsion are exactly balanced, it is liquid; and when repulsion predominates, it becomes gaseous.

It is obvious that, since chemical attraction operates between the particles of different bodies, and only when they are at infinitely small distances, the cohesion between the particles of two solid bodies respectively must impede chemical action by preventing the sufficiently close approximation and intermixture of the particles which have affinity for each other. Hence the solid form is most unfavourable to chemical action, although, in rare cases, the power of affinity is sufficient to overcome the obstacle. Thus, phosphorus and iodine, both in the solid form, act powerfully on one another.

But if one or both of the bodies be liquid, the particles of both readily come so near as to admit of affinity producing its full effect. Thus, bromine acts violently on phosphorus, although the latter is solid; nitric acid, in like manner, dissolves metals, and the same acid acts with great energy on alcohol. Indeed, the liquid form is so favourable to chemical action, that the chemist generally endeavours to have one or both of the substances, whose action he wishes to try, in that form.

Moreover, when two solid bodies, as is generally the case, refuse to act on each other, it is commonly sufficient to cause one of them to assume the liquid form. This may be done in two ways; either by applying a sufficient heat to melt it, or by dissolving it in water or some other solvent. Thus iron and sulphur, when mixed in the solid form, do not combine; but if the sulphur be melted by heat, rapid combination takes place. Again: citric acid and carbonate of soda do not act on each other when dry; but if water be added to the mixture, the acid dissolves, and brisk action ensues.

It is evident that heat, being opposed to cohesion, will promote chemical action whenever cohesion or the solid form is the obstacle: and this is the source of the immense value of heat in chemical and manufacturing processes: as, for example, in the smelting of metals from their ores.

But when cohesion has been still further overcome, and the body has assumed the gaseous form, a new impediment is offered to chemical action. The particles, by the predominance of the repulsion due to heat, are now so far removed from each other, as not to come readily within the sphere of chemical affinity. Hence, two bodies in the gaseous form seldom act on one another, unless their mutual attraction be very strong, as in the case of hydrochloric acid gas and ammoniacal gas; or by the aid of heat, light, or electricity, as in the case of chlorine and hydrogen gases. As heat is here the cause of the obstacle, the appropriate remedies are cold and compression, which tend to bring the particles nearer. Heat and electricity are supposed to act by producing compression of some particles in consequence of the expansion of others; but heat certainly acts also by increasing the force of affinity.

Even where only one of the bodies is gaseous, chemical action is much impeded, especially if the other be solid. Still, in many cases, solids and liquids do slowly act on gases; and by such means some of the most important processes in the organic kingdoms are carried on: as, for example, the respiration of animals, and the growth and decay of plants.

In some cases, as in that of hydrochloric acid gas, the affinity between the gas and water is so powerful, that they combine instantaneously when brought into contact.

There are other cases in which solid bodies at the ordinary temperature are incapable of combining with gases, but in which a high temperature, although it opposes chemical action by its tendency to remove still further the particles of the gas, yet, on the other hand, so much exalts the power of affinity as to be the most powerful promoter of combination. The effect of heat in causing wood, coal, or charcoal, to combine with oxygen, as in ordinary combustion, is a familiar example of this: and as, in this form of experiment, the combustion, once begun, produces a great amount of heat without external aid, it is in this manner that heat is obtained and rendered available for the useful purposes above alluded to.

A gaseous body, which under ordinary circumstances will not combine with another substance, may be made to do so, if presented to it in the nascent state, that is, while it is separating from another solid or liquid body. Thus hydrogen gas, if formed in contact with sulphur, will not combine with it; but if the hydrogen be formed by the action of an acid on sulphuret of iron, the sulphur is presented to the gas at the very moment at which the former is separating from the iron, (in the nascent state, as it is called,) and the gas which is now disengaged is a compound of sulphur and of hydrogen.

It sometimes happens that the combination of two bodies is promoted by the presence of a third, which does not combine with either of the two, nor even with the resulting compound. Thus, if oxygen and hydrogen gases be mixed, they do not combine; but the contact of spongy platinum causes their immediate union, although the metal combines neither with oxygen nor with hydrogen, nor with water, the product of their combination.

But in all cases where the third body has a powerful affinity for the resulting compound, its effect in promoting combination is very great, and has got the name of predisposing affinity. Thus, zinc does not decompose water; but if sulphuric acid be added, the water is decomposed, its oxygen uniting with the zinc. In this case, according to the usual explanation, the oxide of zinc formed unites with the acid, and the affinity of the acid for the oxide of zinc is called a predisposing affinity, as if the acid had caused the formation of oxide of zinc because of its affinity for that oxide when formed. In truth, however, all the changes that occur are strictly simultaneous, and the phrase, "predisposing affinity," is not an accurate one. It is, however, sufficiently convenient and expressive to be a good deal used in regard to similar cases.

When two bodies, A and B, are in combination, the force with which they are actually held together is not dependent alone on their mutual affinity, but also on their relative mass. In the compound ABB, A is retained by a greater force than in AB. This is the result of the increased mass of B. Or we may view it thus:—In the compound AABB, the first A may be removed with comparative facility, the relative masses of A and B being equal. But after the removal of the first A, the mass of B is relatively doubled, and the second A requires for its removal a much greater force. It is obvious that, conversely, in ABB, the second B is less forcibly retained than the B in AB.

When a body, A, is presented to two bodies, B and C, for each of which it has affinity, although unequal, then, if nothing interfere, A will divide itself between B and C, according to its affinity for each. But the effect of mass is seen here also; for if the mass of C, the body for which A has least affinity, be much larger than that of B, then the division will be no longer in the ratio of the affinities to A, but C will obtain more, and B less, of A.

When to a compound body, AB, another body, C, is added, having an affinity for B, both combination and decomposition occur: for AB is decomposed, and at the same time B, which separates from A, enters into combination with C. It does not often happen that the mere force of affinity is sufficient to complete such a change, but such cases do occur: as where iron acts on a salt of copper, or copper on a salt of silver, the one metal taking the place of the other, and the latter being entirely separated. More frequently a part only of B is separated from A and combines with C; and thus there are present, at the same time, the compounds AB and BC, while part of A and of C exists in the free or uncombined state along with them.

If now the free A be removed from the mixture, the free C, being unresisted, at last effects a complete separation of A. The removal of the free A is effected either when that body assumes the solid form by virtue of its great cohesion, or when it takes the form of gas in consequence of its feeble cohesive power, or of the application of heat. The precipitation of an insoluble oxide by a soluble alkali is an example of the former; the formation of glass by the fusion of silicic acid with carbonate of potash is an illustration of the latter case. Similar cases are of constant occurrence.

In both cases, the decomposition is the more easy and complete, the larger the mass of the decomposing body C employed. And from this follows the curious fact, that if, in any given temperature, we can alter the form or the mass of either of the bodies which act on one another, the result of the experiment is likewise altered: nay, it may actually be reversed. Thus, if oxide of iron be exposed at a red-heat to a current of hydrogen gas, the oxide is decomposed, its oxygen, with the hydrogen, forming water, while the iron is reduced to the metallic state.

But if now the iron be heated red hot, and exposed to a current of the vapour of water, the water is decomposed, its oxygen, with the iron, forming oxide of iron ; while the hydrogen is reduced to the free state.

Decomposition is rendered complete, not only when the body A, which is separated, assumes the sold form, but also when A remains liquid or dissolved, and the new body, BC, takes the solid form, or is insoluble. Hence the nature of the liquid, in which a chemical action goes on, exerts a most important influence on the result of the action.

When two compound bodies, AB and CD, act on one another, both decomposition and combination occur. When complete, the change is called double decomposition, since both AB and CD are decomposed ; but at the same time the two new combinations, AD and CB, have been formed. Should the change be only partial, the four compounds AB, CD, AD and CB, will be present together. Double decomposition is of very frequent occurrence.

In cases where a compound, AB, cannot be decomposed by a body, C, even with the aid of a high temperature, the addition of a fourth body, D, if it have an affinity for A, while there is an affinity between C and B, will often enable us to accomplish the decomposition. Thus, oxide of aluminum cannot be decomposed by charcoal even at a white-heat : but when a current of chlorine gas is passed over the mixture, the chlorine, by virtue of its affinity for aluminum, added to that of carbon for oxygen, effects the decomposition, and we obtain chloride of aluminum and oxide of carbon.

When a compound of three or more elements is exposed to a high temperature, the elements unite to form such new compounds as are not decomposable by the temperature employed.

If such a compound be heated along with a body which is capable of forming with some of the elements in certain proportions a more fixed compound, the remaining elements give rise to one or more new and more volatile compounds.

The two last are the principal laws which regulate the phenomena of the destructive distillation of organic substances.

Such are the most important facts in regard to the circumstances under which combination and decomposition occur. We now come to the subject of the proportions in which bodies combine together, or

Combination in Definite Proportions.

The experience of chemists, derived from many thousand analyses, has established the following laws; which, however, are purely the expression of ascertained facts, and involve no hypothesis whatever:—

1. The quantity, by weight, of the body B, which is taken up by a given weight of the body A, to produce the compound AB, is definite and unchangeable. Thus 8 grains of oxygen are invariably taken up by 1 grain of hydrogen (in round numbers) to produce water: or, in other words, 9 grains of water are invariably composed of 8 grains of oxygen and 1 of hydrogen.

2. When a body A combines with a body B in more proportions than one, producing more than one distinct compound, the quantity, by weight, of B, which is united to the same weight of A in the different compounds, increases according to one of two ratios. According to one, the series of compounds formed is—

A + B,	1st compound	. .	B = 1
A + BB,	2nd do.	. .	B = 2
A + BBB,	3rd do.	. . .	B = 3
A + BBBB,	4th do.	. .	B = 4
A + BBBBB,	5th do.	. . .	B = 5

According to the other, the series of compounds is—

A + BBB,	1st compound	.	A : B = 1 : 3
A + BBBBB,	2nd do.	. .	A : B = 1 : 5
A + BBBBBBB,	3rd do.	. .	A : B = 1 : 7

The compounds of nitrogen and oxygen offer an example of the first series of multiple proportions. In the first of these compounds,

	14	grs. of nitrogen	are united	with	8	of oxygen.
In the 2nd.	14	,,	,,	,,	16	,,
,, 3rd.	14	,,	,,	,,	24	,,
,, 4th.	14	,,	,,	,,	32	,,
,, 5th.	14	,,	,,	,,	40	,,

The compounds of arsenic and oxygen will illustrate the second series. In the first of these compounds,

	75·4	grs. of arsenic	are united	with	24	of oxygen.
In the 2nd.	75·4	,,	,,	,,	40	,,

Here the quantities of oxygen increase in the ratio of 3 to 5.

3. The proportions, by weight, in which bodies combine, are proportional to each other. That is: if a given weight of A unite with weights of B and C, which are to each other as 3 to 4, for example; then if a fourth body, D, unite with B and

with C likewise, the weights of B and C combined with D will also be to each other as 3 to 4.

Thus, 100 grs. of potassium unite with 20·41 grs. of oxygen; 100 grs. of potassium unite also with 41·06 grs. of sulphur. Now 100 grs. of silver unite with 7·39 grs. of oxygen, and also with 14·88 grs. of sulphur. According to this law, we find that 7·39 : 14·88 : : 20·41 : 41·06; or, in other words, that the weights of oxygen and sulphur which unite with 100 grs. of silver bear to each other the same proportion as the weights of those elements which combine with 100 grs. of potassium.

Another consequence of this law is, that the weights of two bodies which combine with the same weight of a third body, will also represent the weights of these two bodies which unite together, if they are capable of combination; or if the proportions should not be precisely the same, they will be found to be multiples or submultiples of those weights.

Thus, 8 grs. of oxygen combine with 1 grain of hydrogen to form water; and 8 grs. of oxygen combine with 16 of sulphur to form hyposulphurous acid. Now, sulphur and hydrogen combine together to form hydrosulphuric acid; and that compound is found to contain sulphur and hydrogen in the proportion of 16 grs. of the former to 1 grain of the latter. The same elements form another compound, the persulphuret of hydrogen; and in this the proportions are 32 of sulphur to 1 of hydrogen. Now $32 = 16 \times 2$.

If, therefore, we know the weights of two bodies, B and C, which combine with a given weight of A, we also know the relative weights in which, or in multiples or submultiples of which, B and C will combine together.

Now oxygen is capable of uniting with all the other elements, (save perhaps with fluorine); and therefore if we ascertain by experiment the weights of the different elements which combine with a given weight of oxygen, the weights thus obtained will inform us, not only in what proportions (or their multiples) these elements combine with oxygen, but also in what proportions (or their multiples) they combine with each other, provided they are capable of doing so.

It is obviously of no importance what number we select to represent the standard weight of oxygen, to which the other elements are referred. On the Continent 100 is usually taken, and the combining numbers of the other elements are referred to oxygen as 100. In this country, for the sake of convenience in calculation, advantage has been taken of the fact that the combining weight or number of hydrogen is the smallest of all, and hydrogen has consequently been made the standard, with the number 1. Now as 1 of hydrogen is found to combine (in water) with 8 of oxygen, it is obvious that if hydrogen be represented by 1, oxygen will be represented by 8. Again, on the Continental scale, oxygen being 100, hydrogen must be $\frac{100}{8}$ = 12·5, the proportion being preserved exactly the same. So that it is equally correct to say that water is composed of 100 grs. of oxygen, combined with 12·5 of hydrogen, and to say that water consists of 8 grs. of oxygen and 1 of hydrogen. Both scales are so extensively employed, that the chemist ought to be familiar with both, and, accordingly, both are subjoined. It is hardly necessary to point out that the numbers of the scale in which oxygen = 100, which we shall call the oxygen scale, may be easily reduced to those of the other, or hydrogen scale, in which oxygen = 8 by dividing the former by 12·5, and that conversely the numbers of the hydrogen scale if multiplied by 12.5, are converted into those of the oxygen scale.

The numbers, then, attached to the names of the elements in the subjoined Table, are the results of experience, and merely represent the relative weights of the elements which (or multiples of them) combine with 100 of oxygen on the one scale, and with 8 of oxygen on the other. In this work we shall use the numbers of the hydrogen scale : but the table of the other scale will be of use to those who read foreign chemical works ; and the numbers of one scale may at any time be substituted for those of the other, provided we do not mix them up together.

TABLE OF COMBINING PROPORTIONS.

Elements.	Symbols.	Oxygen. = 100.	Hydrogen. = 1.	Elements.	Symbols.	Oxygen. = 100.	Hydrogen. = 1.
Aluminum	Al	171·17	13·72	Mercury (Hydrargyrum)	Hg	2531·65	202·87
Antimony (Stibium)	Sb	806·45	64·62	Molybdenum	Mo	598·52	47·96
Arsenic	As	470·04	37·67	Nickel	Ni	369·68	29·62
Barium	Ba	856·88	68·66	Nitrogen	N	177·04	14·19
Bismuth	Bi	886·92	71·07	Osmium	Os	1244·49	99·72
Boron	B	136·25	10·91	Oxygen	O	100·00	8·013
Bromine	Br	978·30	78·39	Palladium	Pd	665·90	53·36
Cadmium	Cd	696·77	55·83	Phosphorus	P	196·14	15·72
Calcium	Ca	256·02	20·52	Platinum	Pt	1233·50	98·84
Carbon	C	75·40	6·04	Potassium (Kalium)	K	489·92	39·26
Cerium	Ce	574·7	46·05	Rhodium	R	651·39	52·20
Chlorine	Cl	442·65	35·47	Selenium	Se	494·58	39·63
Chromium	Cr	351·82	28·19	Silicon	Si	277·31	22·22
Cobalt	Co	368·99	29·57	Silver (Argentum)	Ag	1351·61	108·31
Columbium (Tantalum)	Ta	2307·44	184·90	Sodium (Natrium)	Na	290·90	23·31
Copper (Cuprum)	Cu	395·7	31·71	Strontium	Sr	547·29	43·85
Fluorine	F	233·80	18·74	Sulphur	S	201·17	16·12
Glucinum	G	331.26	26·54	Tellurium	Te	801·76	64·25
Gold (Aurum)	Au	2486·02	199·2	Thorium	Th	744·90	59·831
Hydrogen	H	12·479	1·00	Tin (Stannum)	Sn	735·29	58·92
Iodine	I	1579·50	126·57	Titanium	Ti	303·66	24·33
Iridium	Ir	1233·50	98·84	Tungsten (Wolfram)	W	1246·25	99·70
Iron (Ferrum)	Fe	339·21	27·18	Vanadium	V	856·86	68·66
Lead (Plumbum)	Pb	1294·50	103·73	Uranium	U	2711.36	217·2
Lithium	L	80·33	6·44	Yttrium	Y	402·51	32·25
Magnesium	Mg	158·35	12·89	Zinc	Zn	403·23	32·31
Manganese	Mn	345·89	27·72	Zirconium	Zr	420·20	33·67

The number 39, attached to potassium,* expresses the fact that 39 grains of potassium combine with 8 of oxygen, and 16 of sulphur : 8 and 16 being the numbers respectively attached to oxygen and sulphur.

These numbers further express the facts, that if we wish to convert 47 grains of oxide of potassium, composed of 39 of potassium and 8 of oxygen, into sulphuret of potassium, 16 grs. of sulphur will be required to displace the 8 of oxygen, and will give 55 grains of sulphuret.

We thus perceive that 16 grains of sulphur are the equivalent of 8 grains of oxygen. Hence the term " equivalent " is used as synonymous with combining proportion, and we shall in this work employ the term equivalent by preference.

When an element combines with oxygen in only one proportion, the equivalent of that element is the weight which combines with 8 (or on the other scale with 100) of oxygen. Or we may calculate the equivalent from the compound, if there be one, of the element with chlorine.

Thus, in the oxide of potassium (potash), 39 grs. of potassium are combined with 8 of oxygen. If there were no other compound of potassium and oxygen, we should take 39 for the equivalent of potassium. But there is another compound of these elements, and in order to acquire certainty, we refer to the compound (there is but one) which potassium forms with chlorine. We find this to contain 39 grs. of potassium, and 35 of chlorine ; and as 35 is the equivalent of chlorine, we conclude that 39 is the true equivalent of potassium.

Where an element combines with oxygen in several proportions, we are more uncertain. If the proportions of oxygen belong to the series of simple multiples, the equivalent is usually calculated from that compound which contains least oxygen, assuming that to contain an equivalent of oxygen.

Thus nitrogen forms 5 compounds with oxygen. In the first 14 grs. of nitrogen are combined with 8 of oxygen ; in the fifth, 14 grs. of nitrogen are united with 40 of oxygen. Taking the former, we conclude 14 to be the equivalent of nitrogen ; but if we selected the other, then the equivalent of nitrogen would necessarily be five times smaller. On the ordinary view, we consider the fifth compound to consist of one equivalent of nitrogen$=14$, and 5 equivalents of oxygen$=8\times5=40$. But it will be seen that this is, to some extent, arbitrary ; and that we might consider the fifth compound as formed of one equivalent of each, and the first as composed of one equivalent of oxygen, and 5 of nitrogen.

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* Here the fractions, for convenience, are omitted.

The usual system of equivalents, above explained, being consistent and uniform, as far as possible, is very convenient; but the student must remember, that while the combining proportions are fixed, it is, in any one compound, a matter of arbitrary choice, whether it be viewed as containing one or more equivalents of any element.

A very large proportion of elements, however, combine among each other according to laws so simple, that when we have assumed 8, for example, to represent one equivalent of oxygen, we need have no doubt as to the equivalents of the other elements.

In those compounds of one element with two or three proportions of another, where the quantities of the latter are not simple multiples, but belong to the series 3 : 5 : 7, much greater uncertainty prevails as to the equivalents. Thus, arsenic, antimony, and phosphorus, form compounds with oxygen, chlorine, and sulphur, belonging to this latter series; and chemists are not fully agreed whether they ought to consider the quantity of arsenic, antimony, or phosphorus, which combines with 3 or 5 equivalents of oxygen, chlorine, and sulphur, as representing one equivalent, or two equivalents. The same doubt occurs in other cases; and we are guided, in such instances, chiefly by probabilities, and by the rule to avoid, as much as possible, fractions of equivalents. Thus, if we suppose the first oxide of arsenic to contain 1 equivalent of arsenic, and 1 of oxygen, the second must contain 1 equivalent of arsenic, and $1\frac{2}{3}$ equivalent of oxygen. We, therefore, prefer to consider the first as formed of 2 eq. arsenic, and 3 eq. oxygen; and the second as formed of 2 eq. arsenic, and 5 eq. oxygen. There is still a third way, by which also fractions may be avoided; and that is, to make the first a compound of 1 eq. arsenic, and 3 eq. oxygen; and the second a compound of 1 eq. arsenic, and 5 eq. oxygen. This last view, however, does not in many cases agree so well as the preceding, with the composition of the other compounds of the same element.

It is to be observed, that whichever view is adopted, the facts of the proportions remain unchanged. It is only the equivalent of arsenic which requires to be altered.

The equivalent of a compound body is the sum of the equivalents of its component parts. Thus, potash being composed of 1 eq. of potassium, 39, and 1 eq. of oxygen, 8, its equivalent is $39+8=47$. Sulphuric acid is composed of 1 eq. of sulphur, 16, and 3 eq. of oxygen, 24; and, consequently, its equivalent is $40=16+24$ As in the case of elementary bodies, the equivalents represent the combining proportions. Thus, the neutral sulphate of potash contains 47 grs. of potash, and 40 grs. of sulphuric acid. The law of multiples also applies to compound bodies; for there is another compound of sulphuric acid and potash, the bisulphate of potash, in which 47 grs. of potash are combined with 80 grs. of sulphuric acid, or 1 eq. of potash with 2 eq. of the acid.

The use of equivalents enables us to define more accurately some of the more important classes of compounds.

Oxygen acids are compounds of one or two equivalents of the metalloids, and of certain metals, with two or more equivalents of oxygen.

Oxygen bases are, without exception, compounds of metals with oxygen. In most cases, the base contains 1 eq. of the metal, and 1 eq. of oxygen; in a few bases there are two eq. of the metal, and 3 eq. of oxygen; and in one or two there are two eqs. of metal to 1 eq. of oxygen.

A neutral salt is a compound of 1 eq. of an oxygen acid, with 1 eq. of a base; or a compound of 1 eq. of a metal with 1 eq. of the radical of a hydrogen acid. Thus neutral sulphate of potash contains 1 eq. of sulphuric acid, and 1 eq. of potash; while common salt is composed of 1 eq. of sodium, and 1 eq. of chlorine.

A hydrogen acid is, in almost every case, composed of 1 eq. of hydrogen, and 1 eq. of a radical, simple or compound. Thus hydrochloric acid is composed of 1 eq. of hydrogen, and 1 eq. of chlorine; and hydrocyanic acid is formed of 1 eq. of hydrogen, and 1 eq. of the compound radical cyanogen.

The equivalent of an acid is that quantity which will form a neutral salt with one equivalent of a base; and, in like manner, the equivalent of a base is that quantity which forms a neutral salt with one equivalent of an acid.

The equivalent of potash is 47. Now, in order to form a neutral salt with 47 grs. of potash, 54 grs. of nitric acid must be added: 54 is, therefore, the equivalent of nitric acid. Again, 40 is the equivalent of sulphuric acid; and in order to form a neutral salt with 40 grs. of sulphuric acid, 31 grs. of soda are required. Hence, 31 is the equivalent of the base, soda or oxide of sodium.

Since the equivalent of a compound body is the sum of the equivalents of its constituents, it follows, that if we know the equivalent of a compound and the relative proportions by weight of its component parts, we can calculate the *number* of equivalents of each element contained in the compound. For example, we find by analysis, that 100 grs. of hyposulphuric acid are composed of 44·59 grs. sulphur, and 55·41 grs. oxygen. We also find, by experiment, that the equivalent of hyposulphuric acid is 72. Now, in order to ascertain the number of equivalents of sulphur and oxygen contained in the acid, we first examine how much sulphur and oxygen are present in 72 grs. of the acid. It is clear, that if 100 grs. contain 44·59 of sulphur, 72 will contain 32 of sulphur; and the remainder, 40, must be oxygen. But 32 is equal to 2 eq. of sulphur, the equivalent of sulphur being 16; and 40 is equal to 5 equivalents of oxygen, or 5 times 8. Hence the acid in question is composed of two eq. of sulphur, combined with 5 eq. of oxygen.

The rule for the above calculation is to ascertain the proportions of the elements in the equivalent number of the compound; and as these proportions represent respectively the sums of the equivalents of the elements, to divide the numbers by the equivalents. In the above case, 32 (the proportion of sulphur in 72, the equivalent of the acid)÷16=2 eq. of sulphur; and 40 (the proportion of oxygen in 72 of the acid)÷8=5 eq. of oxygen.

In cases where we have ascertained the proportions of the elements in a compound, but are ignorant of its equivalent or combining proportion, we cannot determine with certainty the absolute, but only the relative number of equivalents contained in the compound. For example, it is shown by analysis that 100 grs. of sugar of milk contain—

Carbon	40·45
Hydrogen	6·61
Oxygen	52·94
	100·00

But as sugar of milk enters into hardly any combinations, we cannot ascertain its combining proportion or equivalent, and thus it is, of course, impossible to tell how many equivalents of carbon, hydrogen, and oxygen, are contained in 1 eq. of sugar of milk. But we can ascertain the relative numbers of equivalents as follows. Divide the weight of carbon in 100 parts of sugar of milk by the equivalent of carbon, which is 6 : 40·45÷6=6·74. Next, divide the weight of hydrogen in 100, which is 6·61, by the equivalent of hydrogen, which is 1 : 6·61÷1=6·61. Lastly, divide 52·94, the weight of oxygen in 100, by 8, the equivalent of oxygen. 52·94÷8=6·61. Here, then, the relative numbers of equivalents of carbon, hydrogen, and oxygen, are represented by the numbers 6·74, 6·61, and 6·61: or, making allowance for the unavoidable errors of manipulation, there is an equal number of equivalents of each. We cannot say whether sugar of milk contains 1, 2, 3, 4, 6, 12, or any other number of equivalents of each of its elements; we only know that if 1 eq. of sugar of milk contains 6 eq. of carbon, it must likewise contain 6 of oxygen and 6 of hydrogen.

When a body, A, combines with B and C, and the number of equivalents of B and of C, which respectively unite with 1 or more equivalents of A is equal, the compounds A B and A C are said to correspond in constitution, or they are called corresponding compounds. Thus, 1 eq. of potassium combines with 1 eq. of oxygen, and 1 eq. of potassium combines with 1 eq. of chlorine, and we say that chloride of potassium and protoxide of potassium (potash) are the corresponding chlorine and oxygen compounds of that metal.

When two compounds, A B and C D, respectively consist of an equal number of equivalents, they are said to be proportional compounds. Thus, oxide of potassium contains 1 eq. of oxygen and 1 eq. of potassium; hydrochloric acid contains 1 eq. of hydrogen and 1 eq. of chlorine; and we say that the composition of hydrochloric acid is proportional to that of oxide of potassium (potash).

When two proportional compounds mutually decompose each other, the resulting compounds are likewise proportional; and we have a complete case of double decomposition. Thus 1 eq. hydrochloric acid and 1 eq. oxide of potassium, act on each other, and give rise to water (1 eq. oxygen and 1 eq. hydrogen) and to chloride of potassium (1 eq. chlorine and 1 eq. potassium), which new compounds are obviously proportional. Any excess of either of the original compounds, beyond the 1 eq. required, remains undecomposed, and mixes with the new compounds.

When two bodies act on one another, which are not proportional, they may do so in the proportion of one equivalent of each, or in the proportion of 1 eq. of the one compound to 2 or more of the other.

In the former case there may be formed—

1. Two new compounds, not proportional to each other but corresponding respectively to the two original compounds, or—
2. Two new proportional compounds, in which case one of the elements of one of the original compounds must be partially separated.

We may thus have

1. A B + C D D producing A C + B D D

or,

2. A B + C D D producing A C + B D + D

In the latter case there may be formed—

1. An equal number of new compounds, not proportional, but corresponding to the original compounds.
2. Two new compounds, proportional to each other, in which case an element has been partially separated.
3. Two new compounds, not proportional, and one of which does not even correspond to either of the original compounds. Here also an element has been partially separated.

We may thus have

1. A + 5 B and 5 C D producing A + 5 C and 5 B D.
2. A + 2 B and 2 C D producing A C, 2 B D, and C.
3. A + 5 B and 5 C D producing A + 3 C, 5 B D and 2 C.

Numerous examples of these and of many similar modes of decomposition will occur in the course of this work. For the present, our space makes it necessary to confine ourselves to the general statements.

Under all circumstances, and in the most complicated chemical changes, the composition of the new products must admit, when expressed in equivalents, of a distinct relation being traced to the composition of the compounds from which these products have been derived. It is to the steady application of this principle to the investigation of the complicated decompositions of organic compounds, that we must ascribe the amazingly rapid progress which has of late been made in organic chemistry.

It is obvious that where we are unable to trace the relation above mentioned between the products and the substances which yield them, this must be looked upon as a proof that we do not yet fully understand the changes we are investigating; and that we are either mistaken in the composition which our analyses lead us to assign to one or more of the new compounds, or have overlooked some one or more of the products actually formed.

The laws of combination which have been briefly indicated in the foregoing pages, have been deduced from accurate observation, and are nothing more than an abridged expression of facts. They are consequently entirely independent of any theory or explanation of their causes which may be attempted. Neither is it necessary to attempt any such theory or explanation, since, for all practical purposes, the facts alone are required.

But the human mind is never satisfied with observing and ascertaining facts, and deducing from them those general expressions which are called laws of nature. Man ever strives to account for, to explain, that which he has observed: and although his explanations never reach the essence of things, but only enable him to generalise to a greater extent, and to approach somewhat more nearly the Great First Cause of all, still it appears to be a law of his intellect, that he shall never cease from his attempts to explain, by reference to some simple principle, the complicated phenomena by which he is surrounded.

The facts of gravitation are well known, and entitle us to admit the law, that all material bodies have a tendency to move towards each other with a force which is proportional to their masses, and which varies inversely as the squares of their distances. To account for this, we are in the habit of assuming the existence of a certain force which we call the attraction of gravitation. But we know nothing of the nature of this force; and, assuming its existence, it is only known to us by its effects. Nor does the assumption enable us to understand *how, in what way*, it acts in attracting masses of matter towards each other.

But if we assume the existence of such a force, acting according to the above law, then we can deduce, as necessary inferences from these data, all the phenomena which have been observed, and many which have not been observed, but which we are thus enabled to anticipate. There is, therefore, an obvious advantage in assuming the existence of this supposed cause, as we are thus enabled to remember and to classify the phenomena much better than in the form of a dry catalogue of facts, not attached to any common idea.

If, in like manner, we seek for some hypothesis, which shall account for the facts of combination in definite and multiple proportions, the first obvious conclusion is that the cause of these phenomena must be intimately connected with the mechanical constitution of matter. But since our senses are not capable of directly taking cognisance of the ultimate physical constitution of matter, and since the ultimate causes of natural phenomena are also beyond the reach of our senses, we must have recourse to induction from facts, or to some hypothesis regarding the constitution of matter, which may serve to explain the phenomena.

Different opinions have been held as to the constitution of matter; but two in particular have prevailed. According to one, matter is susceptible of being divided *ad infinitum*: according to the other, matter is formed of particles, which are indeed very minute, far too minute to be cognisable by our senses; but which still possess a definite size, and cannot be divided. They are hence called *atoms*.

Now it is very remarkable, that if we assume the latter view, or that which is called the atomic constitution of matter, to be correct, and if we further assume that the individual atoms of different elements possess different weights, but always the same weight in the same element, we can from these data, deduce all the facts of combination in definite and multiple proportions. This is the theory proposed by Dalton —The Atomic Theory.

No other hypothesis hitherto proposed is capable of explaining the phenomena ; and therefore in the present state of our knowledge, and until a better explanation shall be given, we may admit the atomic theory. It is to be observed, however, that we have no positive proof of its truth, nor are we likely to obtain such proof. On the other hand, the discovery of any fact inconsistent with the atomic theory would compel us to reject it, even if we had no other theory to supply its place. But whether the atomic theory be admitted or not, the facts of combination in definite and multiple proportions remain unaffected.

Atomic Theory.

According to the atomic hypothesis, therefore, matter is composed of certain minute, indivisible particles, or atoms ; and consequently cannot be divided infinitely. We may divide a mass of matter to a very great extent, far beyond the point at which our senses cease to be able to follow ; but still there is a limit to divisibility, and we should reach that limit if we succeeded in dividing so far that the resulting particles were the individual atoms.

Here it may be observed, that the partisans of the opinion according to which matter is infinitely divisible argue thus : there is no conceivable particle of matter so small that we cannot conceive it to be divided into two halves, and so on *ad infinitum :* therefore there is no limit to the divisibility of matter.

Now while we admit that there is no limit to *our conception of* the divisibility of matter, this does not prove that there may not be a limit, in point of fact, to its actual divisibility. For, let us consider a moment what division really is ; and we shall find that it can only be defined as the separation of one portion of matter from others. Now as matter, in its usual forms, undoubtedly consists of particles held together, more or less firmly, by cohesion, it is plain that we can easily, by overcoming cohesion, separate those particles from each other ; and this is ordinary division.

But, on the atomic hypothesis, each of these visible ordinary particles is, like the original mass, formed of still smaller particles cohering together, but, in neither case, in absolute contact. Indeed, the phenomena of expansion by heat, and contraction by cold, demonstrate that the particles of matter are not in absolute contact: in other words, an ordinary mass of matter may be defined as *a portion of space not entirely filled with matter.*

Let us now define an atom as *a portion of space entirely filled by matter*, and we see at once that such a mass cannot possibly admit of division. It is strictly a unit, and as division implies separation of one unit from another, it is here evidently impossible. It is not meant that we can prove this to be the nature of atoms, for we cannot even prove their existence: but the object of the above illustration is to show that we can conceive the existence of an indivisible particle, and therefore that the argument above described in favour of the infinite divisibility of matter is not necessarily conclusive.

Such a particle or atom as has now been defined, or, in other words, a single portion of matter entirely filling the space bounded by its circumference, cannot be cut in two, like a mass of matter, for there is no interstice into which, as in ordinary matter, the edge of a cutting instrument can penetrate; and it cannot, being a unit, be separated from itself. It cannot be crushed to powder, for the particles of a powder existed previously as distinct particles, in the solid mass of matter, and were only separated by the force employed. It cannot be drawn out like metal into wire, or beat out into thin leaves: for both drawing out and beating out are merely new *arrangements* of a plurality of particles, and we have here only a unit.

Moreover, such a particle or atom would, in all probability, be spherical, since no reason can be assigned why one dimension should exceed another. It would no doubt be opaque; for transparency is the result of the passage of light through the vacant spaces between the particles of matter: and colourless, because colour depends on the action of the particles of matter on light; and it would be perfectly hard.

In short, it is evident that we can imagine indivisible atoms to exist; and that the physical properties of matter are not in any degree inconsistent with the idea that it is made up of such atoms.

The atomic hypothesis goes on to assume that the atoms of the different elements possess different weights, but that those of the same element possess invariably the same weight.

The third assumption is, that when one element unites with another, the atoms of the two respectively combine. Thus, an atom of A combines with an atom of B, to form an atom of the compound AB. Or two atoms of A unite with three atoms of B, to form an atom of the compound AABBB.

A distinction must here be made between simple or elementary atoms and compound atoms. It is obvious that an atom of AB, if it contain an atom of A and an atom of B, may be decomposed, and A separated from B. AB is, therefore, not an atom in the fullest sense of the word. But A cannot be separated from B by mechanical means, or otherwise than by chemical agency; so that, in a mechanical sense, AB is an atom, although a compound one. A mass of the compound AB is made up of mechanically indivisible, but chemically divisible, particles of AB, each of which, although it may be called an atom, contains an atom of each of the elements.

The *absolute* weight of the atoms of the different elements is altogether unknown. If, indeed, we had any means of ascertaining the number of atoms in a given weight of any element, in one grain for example, we should know the actual weight of each atom; but this is for the present beyond our power.

But we know the relative weights of two elements which combine to form a given compound; and, therefore, if we assume that the compound contains one atom of each element, we know at once the *relative* weights of the atoms of those elements. Thus, 8 grs. of oxygen unite with 1 gr. of hydrogen to form 9 grains of water; and we assume that water contains 1 atom of each element, or an equal number of atoms of each. In that case it is clear that the relative weights of the single atoms must be the same as those of what are assumed to be equal numbers of each; and, consequently, 1 atom of oxygen will be eight times heavier than 1 atom of hydrogen. If the 8 grs. of oxygen contain 8,000,000 of atoms, then 1 atom of oxygen would weigh $\frac{8}{1000000}$ of a grain, and 1 atom of hydrogen $\frac{1}{1000000}$ of a grain. But although we shall most probably never know the actual number in a given weight, or the absolute weight of the atoms, we are not the less sure that, if matter be composed of atoms, differing in weight for each element, and if water be formed by the union of an equal number of atoms of oxygen and hydrogen, then 1 atom of oxygen must be 8 times heavier than 1 atom of hydrogen.

These numbers, then, express merely the relative weights of these atoms: on the above assumptions, 8 represents the weight of an atom of oxygen, if an atom of hydrogen be supposed to weigh 1: and 12·5 will represent the weight of an atom of hydrogen, if an atom of oxygen be supposed to weigh 100. It is evident that any other numbers might be used, provided the ratio, in this case that of 8 to 1, were kept up.

It is now easy to see, that the atomic hypothesis, if assumed, at once explains all the facts of combination in definite and multiple proportions. As has already been remarked, no other hypothesis, yet proposed, is capable of doing this; and, therefore, while we must not lose sight of the fact that the atomic hypothesis has not been, and indeed probably never will be, demonstrated to be true, we are justified in adopting it, until it shall be proved to be false, or until a better one shall be proposed in its stead.

It will be observed that the weights of the atoms, or atomic weights, as they are termed, coincide with the equivalent numbers previously given. When, therefore, the term atomic weight is used, it is not as implying the established truth of the atomic theory, but only as a convenient synonym for the term equivalent, or for that of combining proportion. Whichever name we use, it must never be forgot that the facts remain unchauged, and are independent of all hypothesis. 9 grains of water invariably contain 8 of oxygen and 1 of hydrogen, whether we speak of the combining proportions, the equivalents, or the atomic weights of oxygen and hydrogen being represented by the numbers 8 and 1. The two former expressions have the advantage of simply expressing the fact without any allusion to hypothesis, and are, therefore, strictly speaking, preferable: but the latter is much used, and may safely be employed when properly defined.

In this country, the terms equivalent and atom have been from the beginning held to be entirely synonymous. On the Continent, this has not been the case: for the equivalent of many elements, such as hydrogen, chlorine, &c., has been there assumed to contain 2 atoms; and hence the atomic weight of hydrogen, for example, has been on the Continent one half of that adopted here.

This is a matter which is, to a great extent, arbitrary, and only affects the mode of viewing and representing the composition of certain compounds. Thus Continental chemists, admitting as we do that 9 grains of water contain 8 of oxygen and 1 of hydrogen, consider water to be composed of 1 atom of oxygen and 2 atoms (= 1 equivalent) of hydrogen; they, consequently, give to hydrogen the atomic weight of 0·5, that of oxygen being 8; or 6·25, that of oxygen being 100.

It is not easy to decide whether water be composed of 1 *atom* of each element, or of 1 *atom* of oxygen to 2 *atoms* of hydrogen. But as both parties agree that water contains 1 *equivalent* of each element, it is obvious that the system adopted in Britain, by which equivalent is made entirely synonymous with atom, has the very great advantage of superior simplicity: and that system will, therefore, be followed in this work. Within the last year or two several of the most distinguished chemists on the Continent have adopted the British system in this respect, and there is little doubt that it will, ere long, become universally prevalent.

The table of equivalents, formerly given, is therefore, at the same time, a table of atomic weights. It is now time to give rules for the use of that table, and particularly for the use of the abbreviations or symbols there attached to the elements, in the construction of formulæ.

Chemical Symbols and Formulæ.

These have nothing in common with algebraical symbols and formulæ. They are mere abbreviations, and are intended to express only the arithmetical operations of addition and subtraction. Various systems have been given to the world: but that which has finally obtained the most extensive currency among the chemists of the day, is one proposed by Liebig and Poggendorff, which we now proceed to explain.

The symbol of an element, standing alone, signifies 1 atom, or equivalent, of the element. Thus O stands for 1 atom of oxygen, H for 1 atom of hydrogen, and Fe for 1 atom of iron (ferrum).

A symbol, with a small figure below and to the right, signifies as many atoms of the element as the figure expresses. Thus O_2 means 2 atoms of oxygen, S_5, 5 atoms of sulphur.

Two symbols joined by the sign +, or simply placed together, signify a compound of 1 atom of each element. Thus $H + O$, or simply $H\,O$, means water, a compound of 1 atom hydrogen, and 1 atom oxygen.

If a figure be attached, as above, to either or both symbols, it multiplies that symbol only to which it is attached. Thus $Mn\,O_2$ is the symbol for peroxide of manganese, a compound of 1 eq. manganese and 2 eq. oxygen. $Cu_2\,O$ is the symbol of suboxide of copper, composed of 2 eq. of copper and 1 eq. oxygen. $Fe_2\,O_3$ is the symbol of peroxide of iron, which contains 2 eq. of iron and 3 eq. of oxygen.

When a compound, formed of two or more compounds, is to be expressed, the compounds which combine are joined, either by a + sign or by a comma. Thus $H\,O + S\,O_3$ or $H\,O, S\,O_3$ both signify hydrated sulphuric acid, a compound of 1 eq. water and 1 eq. dry sulphuric acid.

A large figure, printed on the same level as the symbol, and to the left of it, multiplies every symbol as far as the next comma, or the next + sign; or it multiplies all within brackets if placed before them. Thus $2\,H\,O$ means 2 atoms of water, $2\,S\,O_3, K\,O, H\,O$ represents bisulphate of potash, a compound of 2 eq. sulphuric acid, 1 eq. potash, and 1 eq. water. It might also be written $2\,SO_3 + KO + HO$. But the following, $2\,(SO_3, KO, HO)$ would signify 2 eq. of a compound which was formed of 1 eq. sulphuric acid, 1 eq. potash, and 1 eq. water.

When a compound contains 3 or more elements, the symbols are written simply one after the other, with the necessary figures. Thus, sugar is represented by $C_{12}\,H_{10}\,O_{10}$: that is 12 eq. carbon, 10 eq. hydrogen, and 10 eq. oxygen. Alcohol is $C_4\,H_6\,O_2$.

If we wish to show that any compound of three or more elements really contains two compounds, it is expressed in the following manner: alcohol, $C_4\,H_6\,O_2$, when viewed as a compound of ether and water becomes $C_4\,H_5\,O + HO$. Benzoic ether, $C_{18}\,H_{10}\,O_4$ becomes $C_{14}\,H_5\,O_3$ (benzoic acid) + $C_4\,H_5\,O$ (ether).

In this way we find it quite easy to express in symbols the composition of the most complicated substances. For example, crystallised alum is composed of 1 eq. neutral sulphate of potash, 1 eq. tersulphate of alumina, and 24 eq. of water of crystallisation. This is expressed in symbols, as follows:

$$KO, SO_3 + Al_2O_3, 3SO_3 + 24\,HO.$$

And this abbreviated expression contains, in a line, in addition to the general information concerning alum printed above, more information as to details than could be given in a page of print. It informs us, for example, that alum contains 4 eq. sulphuric acid, of which 1 is combined with 1 eq. of potash, and 3 with 1 eq. of alumina: that alumina is a sesquioxide of aluminum: that 1 eq. alum contains 1 eq. potassium, 2 eq. aluminum, 4 eq. sulphur, 24 eq. hydrogen, and 40 eq. oxygen, &c. &c. &c.

There are, besides the direct information thus conveyed by symbols, two most important uses to which they are applied.

The first is, to render easily intelligible the view taken by a writer of any chemical change, however complicated. This is done by means of a formula or equation: in which all that is essential is, that the sum of the various symbols should be the same on both sides. Thus, to take an example previously described in words (at p. 19), the action of oxide of potassium on hydrochloric acid. This is expressed in a formula as follows:

$$KO + HCl = HO + KCl.$$

Here the symbols on the left are those of the bodies which act on each other, oxide of potassium and hydrochloric acid: while those on the right are the symbols of the new compounds produced, water and chloride of potassium.

Or, to take a more complicated case.

Sugar, $C_{12}H_{10}O_{10}$, when acted on by 6 eq. of hypermanganate of potash, KO, Mn_2O_7, gives rise to 6 eq. of oxalate of potash, KO, C_2O_3, 12 eq. of peroxide of manganese, MnO_2, and 10 eq. of water. All this is briefly and clearly expressed by the equation

$$C_{12}H_{10}O_{10} + 6(KO, Mn_2O_7) = \\ 6(KO, C_2O_3) + 12\,MnO_2 + 10\,HO.$$

The second very important use to which these equations are applied is, that of calculating the quantities of the different substances which must be employed, in order to operate as economically as possible, and likewise the weight of the products which ought to be obtained. Thus, in the last example, we wish to know what proportions of sugar and hypermanganate of potash ought to be used, that nothing of either should be wasted: and also how much oxalate of potash, peroxide of manganese and water will be obtained. By means of the above equation, and the table of atomic weights, we cau easily make all these calculations. Since the equivaleut or atomic weight of a compound is the sum of those of its elements, it is obvious that the equivalent of sugar is equal to the sum of 12 eq. of carbon + 10 eq. hydrogen + 10 oxygen. Now by the table, the equivalent of carbon is 6, that of hydrogen 1, that of oxygen 8. Hence the equivalent of sugar is $= 6 \times 12 + 1 \times 10 + 8 \times 10 = 72 + 10 + 80 = 162$. In like manner the equivalent of hypermanganate of potash is found to be, in round numbers, 160. For every 162 parts, therefore, of sugar, we must employ 6 times $160 = 960$ parts of hypermanganate of potash. The whole materials employed amount to 1122.

On the other hand, we obtain of oxalate of potash, the equivalent of which is (in round numbers) 84, 6 equivalents $= 504$; of peroxide of manganese, the equivalent of which is 44, 12 equivalents $= 528$; and of water, the equivalent of which is 9, 10 equivalents $= 90$; the whole products amounting to 1122.

It is hardly possible to exaggerate the value of so easy a method of representing chemical changes, and of making all the necessary calculations connected with them. Every chemist, and every student of chemistry, ought to be quite familiar with the use of chemical formulæ; and, indeed, without this knowledge it will soon be impossible to read chemical writings. The use of formulæ enables the writer so easily to put before his readers, in a very small space, any conceivable view of the phenomena, such as might require pages to explain in words, that they are now universally employed.

Even in the commonest use of symbols and atomic weights, that, namely, of expressing the composition of any compound, the advantage derived from their employment is immense. Thus, previous to the invention of tables of atomic weights, chemists could only express the composition of a compound by giving the proportions of the elements contained in 100 parts. For example, water, the protoxide of hydrogen, was found to consist of—Hydrogen, 11·11; and oxygen, 88·88, in 100 parts; while the deutoxide of hydrogen was found to consist of—hydrogen, 5·89; and oxygen, 94·11, in 100 parts. It is very difficult for the memory to retain these numbers with accuracy, even in the case of a few such compounds; how much more so, then, must it be to remember the composition of the numerous bodies with which the chemist is constantly occupied!

If, however, we have recourse to symbols, we have only to express the composition of water by HO, and that of the deutoxide of hydrogen by HO_2; and referring to the table of atomic weights, we find that the former contains 1 of hydrogen to 8 oxygen, and the latter, 1 of hydrogen to 16 of oxygen. Even if we could not retain these latter numbers, we should thus still derive great benefit from the use of symbols; but the fact is, that we soon learn the atomic weights of the more important elements, and are not compelled to have recourse to the table for them.

But this is not all; for in the numbers, as given in 100 parts, we can trace no relation; and, consequently, if we commit them to memory, must do so as bare numbers. In the symbols, on the contrary, we see at a glance that the same quantity of hydrogen which, in water, is combined with a given weight of oxygen, is combined with double that weight in the deutoxide of hydrogen; and we are thus supplied, not only with a fact, in itself of the highest value, but also with a link by which the composition of two substances is associated in the memory, and therefore retained with facility.

Before quitting this part of the subject, it is well to point out two results which follow from the atomic theory.

The first is, that since, by definition, an atom is that which cannot be divided, there cannot be formed a compound of 1 atom, or equivalent of one element, and $\frac{1}{2}$ an atom (or any fractional number of atoms, as $1\frac{1}{2}$, $2\frac{1}{2}$, &c.) of another element. Should such proportions appear to exist, they must be so expressed as to get rid of fractions, otherwise they imply a contradiction in terms. Thus, for example, iron combines with oxygen in two proportions. In the first compound, or protoxide of iron, 28 parts (1 eq.) of iron are combined with 8 parts, or

1 eq., of oxygen. We, therefore, assume this compound to contain 1 atom of each element, and express it in symbols by $Fe\,O$. In the other oxide, or peroxide of iron, 28 parts, or 1 eq., of iron are found to be combined with 12 parts of oxygen. Now, 8 being 1 eq. of oxygen, 12 must be $1\frac{1}{2}$ eq. But as it would be absurd to call this oxide a compound of 1 atom of iron and $1\frac{1}{2}$ atom of oxygen, we get rid of the fraction by doubling both numbers, and we represent the peroxide of iron by $Fe_2\,O_3$. Here the proportion is still that of 1 to $1\frac{1}{2}$, but the absurdity of dividing an atom is avoided. It is obvious that the atomic weight of the compound is double what it would be if we had retained the fraction; for $Fe_2=56$, and $O_3=24$: and 56 : 24 : : 28 : 12. As the proportion is still that of 1 to $1\frac{1}{2}$ atom, although there are, in reality, 2 to 3, this compound is frequently called sesquioxide of iron, from *sesqui*, a prefix signifying one and a half. The prefix, *sesqui*, is used in many similar cases, precisely in the same way.

Of course, where analysis indicates the proportions of 1 atom of A to $2\frac{1}{2}$ or $3\frac{1}{2}$ of B, we, in like manner, to avoid fractions, express these proportions by 2 to 5, or by 2 to 7. The symbol for phosphoric acid is $P_2\,O_5$: that of hypermanganic acid is $Mn_2\,O_7$.

The second result or corollary from the atomic theory is, that when two compounds having a common element unite together, the amount of the common element in the equivalent of the one is, to its amount in the equivalent of the other, in a ratio which may be expressed by whole numbers. Thus, potash is composed of potassium and oxygen, sulphuric acid of sulphur and oxygen. Here oxygen is the common element. Now, in an equivalent of potash, KO, there is 1 atom of oxygen$=8$. In an equivalent of sulphuric acid, SO_3, there are 3 atoms of oxygen$=24$; and it is obvious that the oxygen in the latter is to that in the former as 3 : 1. This relation is at once seen in the formula of the compound, sulphate of potash, which is $KO,\,SO_3$; and it prevails necessarily in all neutral compounds of sulphuric acid with bases which have an analogous constitution. In nitrate of potash, $KO,\,NO_5$, the ratio is different, being as 5 : 1. When an acid, such as sulphuric acid, forms a neutral salt with a base of a constitution different from that of potash, as, for example, with sesquioxide of iron, the relation of 3 to 1 is still kept up: for the neutral sulphate of sesquioxide of iron is $Fe_2\,O_3,\,3\,SO_3$. In a compound not neutral, such as $Fe_2\,O_3,\,SO_3$, which represents the basic sulphate of sesquioxide of iron, the relation is different, being that of 3 : 3 or 1 : 1; but still it is capable of being expressed in whole numbers.

COMBINATION BY VOLUMES.

When two gaseous bodies combine together, it is always in such proportions, by volume, that 1 volume of the one gas combines with one or two or more volumes of the other; and if the resulting compound be gaseous, its volume bears some simple ratio to those of its elements. Thus, 1 vol. hydrogen combines with 1 vol. chlorine, to produce 2 vol. hydrochloric acid; and 2 vol. hydrogen combine with 1 vol. oxygen, to form 2 vol. of the vapour or gas of water. It is evident, that where two gases combine in several proportions, the law of multiple proportions must prevail in regard to the volumes as well as in regard to the weights. For example, in the five compounds of nitrogen and oxygen formerly mentioned, 2 vol. nitrogen are combined with 1, 2, 3, 4, and 5 vol. oxygen.

The volume of the compound is in all cases either equal to the sum of the volumes of its component gases, or less than that sum; in the latter case condensation has taken place. It follows that 1 vol. of a compound gas contains either 1 vol. of each of its constituents, or a multiple or a submultiple of a volume of one or both.

It is easy to see that there must be a relation between the volume and the weight of gaseous elements, since the law of definite proportions can be traced in both. Since water, for example, is composed of 8 parts *by weight* of oxygen to 1 of hydrogen, and of 2 parts *by volume* of hydrogen to 1 of oxygen, it must be possible to construct a table of combining volumes, as well as a table of atomic weights; and in fact this may be done in regard to all those elements which may be made to assume the form of gas, and even in regard to some which cannot be obtained in that form, but which combine with gaseous elements to form gaseous compounds.

If the weight of a given volume of oxygen be called 1·000, it will be found that an equal volume of hydrogen will weigh sixteen times less, or 0·0625; and these numbers will represent the relative specific gravities of these gases. But we already know that in water 1 vol. of oxygen is combined with 2 vols. hydrogen; or, taking the specific gravities, 1·000 oxygen with $2 \times 0{\cdot}0625 = 0{\cdot}125$ hydrogen. Now these latter numbers are precisely the atomic weights or equivalents of oxygen and hydrogen, oxygen being made the standard, and = 1·000. Again, 1 vol. hydrogen combines with 1 vol. chlorine to form hydrochloric acid. Now, if 1 vol. hydrogen as above, be represented as weighing 0·0625, 1 vol. chlorine will be found to weigh 2·25; and these numbers are to each other precisely in the ratio of the equivalents of the two gases, which, on the oxygen scale, are 12·5 and 450, or on the hydrogen scale 1 and 36.

It was for a long time supposed, especially among Continental chemists, that equal volumes of the simple gases contained equal numbers of atoms. Were this the case, the specific gravities of the gases compared to oxygen as a standard, would of necessity coincide with the atomic weights as compared with the same standard: and would at all events, whatever standard might be employed, bear the same ratio to each other. Specific gravity in the gaseous form and atomic weight would then be synonymous.

Experiment, however, has demonstrated that this is not the case; but that, while an equivalent of one element is represented by one volume of its gas, two volumes are required to make an equivalent in some cases; and one-half volume, one-third volume, or even less, in others. In the following table will be found the specific gravities or the weights of equal volumes of such elements as admit of their specific gravities being either directly taken or calculated. In the first column are given the usual specific gravities compared to atmospheric air as the standard: in the second the specific gravities compared to hydrogen as the standard, in order to show the relation to the atomic weights:—

Gas or Vapour.	Specific Gravities.		Chemical Equivalents.	
	Air=1.	Hydrogen=1.	By Vol.	By Weight.
Hydrogen. . . .	0·0690	1·00	100	1·00
Nitrogen . . .	0·9727	14·12	100	14·15
Carbon (hypothetical)	0·4213	6·12	100	6·12
Chlorine . . .	2·4700	35·84	100	35·42
Iodine	8·7011	126·30	100	126·30
Bromine . . .	5·3930	78·40	100	78·40
Mercury . . .	6·9690	101·00	200	202·00
Oxygen . . .	1·1025	16·00	50	8·00
Phosphorus . . .	4·3273	62·8	25	15·70
Arsenic . . .	10·3620	150·8	25	37·7
Sulphur . . .	6·6480	96·48	16·66	16·10

It will be observed that the numbers in the second column are not the same in all cases as the equivalent numbers of the elements; but many of them are so, and in these cases a volume represents an equivalent. The other numbers are multiples by a whole number of the equivalent, oxygen being represented, for example, by 16=2+8, and sulphur by 96=6×16. This shows that if an equivalent of hydrogen, chlorine, be represented by 1 vol., an equivalent of oxygen is represented by $\frac{1}{2}$ vol., and an equivalent of sulphur by $\frac{1}{6}$ vol.

The knowledge of the proportions by volume according to which bodies combine, and of the specific gravity of gaseous bodies, enables us to answer a great many questions, and decide a great many doubtful points in Chemistry. Thus—

1. If we know the specific gravity of two simple gases and the proportions by volume in which they combine, we can calculate the composition, by weight, of the compound. Thus, 2 vols. of hydrogen combine with 1 vol. of oxygen to form water. Now, the Sp. G. of hydrogen (Air = 1·000), is 0·0694, and that of oxygen is 1·1111. Therefore water is composed, by weight, of 0·0694 × 2 = 0·1388 of hydrogen, and 1·1111 of oxygen.

2. If we know the volumes of the elements of a compound, and their specific gravities, and the volume of the compound, we can calculate the Sp. G. of the compound. To take the same example, 2 vols. hydrogen, Sp. G. = 0·0694, and 1 vol. oxygen, Sp. G. = 1·1111, combine to form 2 vols. vapour of water. Now the vapour of water must weigh as much as the oxygen and hydrogen taken together, that is, 0·0694 × 2 + 1·1111 = 1·2499. But as this represents the weight of 2 vols. vapour of water, the weight of 1 vol. vapour of water (or the specific gravity) must be 1·2499 ÷ 2 = 0·6249.

3. If we know the volume and the Sp. G. of one of the two elements of a binary compound, and the Sp. G. of the compound itself, we can calculate the composition, by weight, of the compound. Thus, 1 vol. carbonic acid gas contains 1 vol. of oxygen; the Sp. G. of carbonic acid gas is 1·5239, and that of oxygen as before is 1·1111. Subtracting the latter number from the former, we have 0·4128, which must represent the weight of carbon united with 1·1111 of oxygen; and this is the composition, by weight, of carbonic acid gas.

4. If we know the specific gravity of a compound and its composition by weight, we can calculate the composition by volume. Example—by experiment the Sp. G. of the vapour of aldehyde (the weight of 1 vol.) was found to be 1·532; and the analysis of the compound showed that its composition by weight was, carbon 55·024, hydrogen 8·983, and oxygen 35·993, in 100 parts. Now, in order to ascertain the composition by volume, let us calculate the proportions of carbon, hydrogen, and oxygen in 1·532.

If 100 parts contain 55·024 carbon, 1·532 contain 0·84279
„ „ 8·983 hydrogen „ 0·13760
„ „ 35·993 oxygen „ 0·55130

Now, the specific gravity or weight of 1 vol. of carbon is hypothetical or calculated: it is assumed to be 0·42139 (see table): 1 vol. of hydrogen weighs 0·0694, and 1 vol. oxygen weighs 1·1111. It is easy to see, therefore, that 1 vol. of the vapour of aldehyde contains:—

2 vol. vapour of carbon	0·84279
2 vols. hydrogen	0·1388
$\frac{1}{2}$ vol. oxygen	0·5555

It is obvious, therefore, that the knowledge of the volumes in which gaseous bodies combine, and of their specific gravities, is of great value to the chemist: but we must not forget that we have no evidence that equal volumes of different elements contain an equal number of atoms; or, in other words, that the term volume may be substituted for atom or equivalent, as was at one time supposed. On the contrary, all the recent researches on this point go to prove that, in the case of many elements, a volume corresponds to two or more equivalents.

ATOMIC OR EQUIVALENT VOLUMES.

The relation between the atomic weight and the specific gravity of bodies in the gaseous form has been briefly indicated in the preceding section. But the subject admits of being considered under different points of view, according to the notions entertained of the atomic constitution of gases. On the supposition, for example, that the atoms, or ultimate particles of all elementary gases, with their surrounding spheres of heat, possess the same volume, all such gases would contain, in equal volumes, the same number of atoms. But as it is certain that compound gases do not, in all cases, contain the same number of atoms in equal volumes, it is quite possible that elementary gases may also differ in this respect; and, as above stated, the combining volumes of sulphur and of some other elements agree with this conclusion. It is therefore generally admitted that equal volumes of different elementary gases contain different numbers of atoms; that, for example, 1 vol. oxygen contains twice as many atoms, and 1 vol. sulphur (in the form of gas) six times as many atoms as 1 vol. hydrogen, 1 vol. nitrogen, or 1 vol. chlorine.

This obviously implies that the atoms, with their spheres of heat, are of different sizes; and, to take the cases above mentioned, that the atoms of oxygen gas are $\frac{1}{2}$ the size, and those of sulphur $\frac{1}{6}$ the size of the atoms of hydrogen, nitrogen, chlorine, &c. This is what is called the *atomic volume* of gases.

It is not meant that we can ascertain the absolute volume of the atoms, but the relative or comparative volume of the atoms or particles of two or more gases.

Now, since the specific gravity of a gas depends on the number of atoms in a given volume, and on the weight of these atoms, it is evident that the atomic weight, divided by the specific gravity must give the (relative) atomic volume.

For example, let hydrogen be taken as the standard for the specific gravity of gases, as it is for their atomic weights, then the atomic weight of hydrogen, = 1, divided by its specific gravity, = 1, will yield the quotient 1 for the atomic volume of hydrogen. Again, the atomic weight of oxygen, = 8, divided by its specific gravity, = 16, (that of hydrogen = 1) gives the quotient 0.5 or $\frac{1}{2}$, as the atomic volume of oxygen; and the atomic weight of sulphur, = 16, divided by its specific gravity as gas, = 96 (that of hydrogen = 1) gives the quotient 0.1666 or $\frac{1}{6}$, as the atomic volume of sulphur.

We thus see, that, on the supposition above adopted that the atoms of different gases differ in size, we can prove that, whatever be the size of an atom of hydrogen gas, an atom of oxygen gas must be half, and that of an atom of sulphur gas one-sixth that size.

It is further obvious, that the number of atoms in equal volumes must be inversely as the atomic volume; or that the specific gravity of a gas, divided by its atomic weight, will give the number of atoms in a given volume. Hydrogen being retained as the standard, then we have $\frac{1}{1} = 1 =$ the number of atoms in 1 vol. of hydrogen :—$\frac{16}{8} = 2 =$ the number of atoms in 1 vol. oxygen : and $\frac{96}{16} = 6 =$ the number of atoms in 1 vol. gas of sulphur.

More briefly, the atomic volume and the number of atoms are the inverse of each other: so that we have $\frac{1}{6}$ and 6, $\frac{1}{2}$ and 2, 1 and 1.

If, while we make hydrogen the standard of atomic weights, we make air the standard of the specific gravity of gases, then we obtain, as quotients, a series of numbers equally comparable among themselves, but less simple and easy to retain than the above. We should have, for example, $1 \div 0.0694 = 14.409$ for hydrogen; $8 \div 1.1026 = 7.2554$ for oxgen; and $16 \div 6.9000 = 2.3188$, for the atomic volumes of hydrogen, oxygen, and sulphur respectively; and these numbers are to each other as 1, $\frac{1}{2}$, and $\frac{1}{6}$.

In the case of solids and liquids, the relation between atomic weight and specific gravity is far from being so simple, in consequence of the force of cohesion interfering with and disturbing the results. We cannot ascertain whether the atoms of solid bodies have the same size in different bodies, or not; and we cannot tell whether the difference of specific gravity depends on a difference in the number of the atoms, in an equal volume, a difference in the size of the atoms, or a difference in the size of the interstices between the particles, or possibly on two or more of these causes.

Some chemists assume that there are no interstices, but that the atoms wholly fill up the space within the circumference of the body. On this supposition, the atomic weight, divided by the specific gravity (in solids and liquids), must give the atomic volume. It is difficult, however, to admit the absence of interstices or pores in solids and liquids, if we consider them formed of atoms; and it is perhaps better to use the term *equivalent volume* instead of *atomic volume.*

The equivalent volume, then, of a solid or liquid is obtained by dividing the atomic weight (or rather equivalent number) by the specific gravity in the solid or liquid state. Water, the standard for the specific gravity of liquids and solids, may be made the standard of equivalent volumes.

Thus the atomic weight of water, = 9, divided by its specific gravity, = 1, gives the quotient 9 as its equivalent volume. The atomic weight of potassium, 39·26, divided by its specific gravity, 0·865, gives 45·387 for its equivalent volume; and the atomic weight of carbon, 6·04, divided by its specific gravity in the form of diamond, = 3·5, the quotient 1·725 for the equivalent volume of the diamoud.

On the other hand, the specific gravity, divided by the atomic weight, gives the relative number of atoms in a given volume; and in the case of potassium this is 0·865 ÷ 39·25 = 0·0220; in the case of carbon it is 3·5 ÷ 6·04 = 0·5794. Finally in the case of water, the relative number of atoms in a given volume, which may be made the standard, is 1 ÷ 9 = 0·1111. If, for convenience, the number for water is made 1000, then that for potassium becomes 198·0, and that for carbon becomes 5215.

Assuming, likewise for convenience, the equivalent volume of water (the standard) to be, (instead of 9) 1000, the equivalent volume of potassium becomes 5043, and that of carbon 191·666.

We thus perceive that the equivalent (or atomic) volume of carbon is about twenty-five times less than that of potassium, and that the number of atoms of carbon contained in a given volume is about twenty-five times greater than in the case of potassium. This compression of so large a number of atoms into a given volume may be the cause of the great hardness of the diamond.

The whole subject of equivalent volumes is full of interest; but as chemists have only recently begun to study solid and liquid bodies in this point of view, our knowledge on the subject is still very imperfect and limited. For what has lately been done, we are chiefly indebted to Kopp and to Schrœder.

Playfair and Joule have very lately published the first part of an elaborate investigation into the volumes occupied by bodies both in the solid form and when dissolved in water; and they have obtained results of an unexpected nature as well as of very great value.

The reader is referred to their paper in the Memoirs of the Chemical Society. Here we have only space to allude to the subject, and to mention that, among other curious results, these chemists have found that many salts, when dissolved in water, do not add to the bulk of the water more than is due to the water actually present in the salts. Thus for example alum, 1 eq. of which contains 23 equivalents of the elements, potassium, aluminum, sulphur, and oxygen, besides 24 eq. of water, dissolves in water without increasing its bulk more than the addition of the 24 eq. of water must necessarily do; so that the 23 eq. abovementioned occupy no additional space, and must either be contained in the pores or interstices of the water, or disappear altogether as far as the occupying of space is concerned, if water be supposed to have no pores.

They have further shown that when salts do add to the bulk of the water in which they are dissolved, the increase of the bulk corresponds to that of a volume, or some multiple of a volume, of water. It is evident that these and similar researches must soon greatly extend our knowledge of the mechanical constitution of matter.

Isomorphism.

Most substances, when they assume the solid form slowly, so as to allow the particles to follow their natural attractions, exhibit, more or less perfectly, a regular form: in other words, they crystallise. Thus carbon, when slowly deposited in the form of diamond, assumes the form of a regular octohedron, or of some form geometrically allied to it; and common salt, a compound body, takes the form of the cube and its modifications, including the octohedron.

Now it has been observed that the same substance invariably crystallises in forms belonging to the same system, but that different substances very frequently present different crystalline forms. Thus, while diamond crystallises in regular octohedrons, iodine forms acute rhombic octohedrons: and while common salt crystallises in cubes, chloride of barium yields right rhombic prisms.

It happens, occasionally, but rarely, that the same element is capable of assuming two crystalline forms, belonging to different systems, and not geometrically connected with each other. Thus sulphur, crystallising from its solution in bisulphuret of carbon, forms very acute rhombic octohedrons, but when melted by heat, and allowed to consolidate by cooling, it yields oblique rhombic prisms.

The same is occasionally observed in compound bodies. Thus, carbonate of lime, in its common form of Iceland spar, crystallises in obtuse rhombohedrons and in innumerable varieties of that form: but in the rarer form of arragonite, it assumes the form of a rhombic prism.

These cases, and others which are analogous, are to be explained by a different arrangement of particles, dependent most probably on a difference of temperature at the period of the formation of the crystals. They are not, however, numerous enough to affect the general law, that the same substance always assumes the same crystalline form.

But the admirable researches of Gay-Lussac and of Mitscherlich have established the fact, that in many instances, different compounds assume the same form. Thus, the following substances, and many others, take the form of the cube, tetrahedron, or regular octohedron, which are geometrically connected. Chloride of sodium (sea-salt), chloride of potassium, sal ammoniac: bromide of potassium: iodide of potassium: sulphuret of lead: fluoride of calcium: bisulphuret of iron: arseniuret of cobalt: sulphate of alumina and potash (alum): ammonia alum: chrome alum, iron alum: sesquioxide of iron, sesquioxide of aluminum, sesquioxide of chromium. In like manner, other crystalline forms are found to be common to many different compounds, although none occurs so frequently as the cube and its congeners.

Now at first sight it would appear that no relation whatever could exist between the form of these numerous and very different compounds, and their composition. But on closer inspection, they are found to arrange themselves into groups. Of these groups, two may be specified among the compounds above enumerated. One is that of the chlorides, bromides, iodides, and fluorides of metals, having the formula MR, that is, 1 at: metal to 1 at: radical. This includes chloride of potassium $K\,Cl$, of sodium $Na\,Cl$, of ammonium (sal-ammoniac) $Am\,Cl$:* to which may be added bromide of potassium $K\,Br$, iodide of potassium $K\,I$, and fluoride of calcium $Ca\,F$: and this group is a very large one. It will be observed that the members of it contain an equivalent of a metal united to 1 equivalent of a metalloid, and are therefore, so far analogous in composition. The next group is that of the alums. Common alum has this formula,

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* See the section on Ammonium.

$$K\,O, S\,O_3 + Al_2\,O_3, 3\,S\,O_3 + 24\,H\,O.$$

Now if we substitute ammonium for potassium, we have

$$Am\,O, S\,O_3 + Al_2\,O_3, 3\,S\,O_3 + 24\,H\,O:$$

and this is the formula of ammonia alum. Chrome alum is

$$K\,O, S\,O_3 + Cr_2\,O_3, 3\,S\,O_3 + 24\,H\,O:$$

and another may be formed by substituting Am for K. Iron alum is

$$K\,O, S\,O_3 + Fe_2\,O_3, 3\,S\,O_3 + 24\,H\,O.$$

And here also another alum is obtained by substituting Am for K. A good many more alums may be procured by substituting Na (sodium) for K, and Mn for Al, that is, manganese for aluminum; and all these salts have the same crystalline form and the same general properties. Here, as in the former more simple group, the analogy in constitution is at once obvious. Every alum is

$$m\,O, S\,O_3 + M_2\,O_3, 3\,S\,O_3 + 24\,H\,O:$$

m stands for a metal of one class, such as potassium, sodium or ammonium: and M for a metal of another class, such as aluminum, iron, chromium or manganese. It appears, therefore, that a salt, containing 1 eq. of a neutral sulphate of a protoxide of one of the former metals ($mO, S\,O_3$), along with 1 eq. of a neutral tersulphate of a sesquioxide of one of the latter metals, (M_2O_3, $3SO_3$), and 24 eq. water (24 HO) takes the crystalline form of common alum, the type of this group. From this we must conclude that the similar *arrangement* of particles prevailing in all these alums is one chief cause of the similarity in form. We see that the particles need not be all identical in two similar crystals; for example, of common alum and of iron alum. But there must be an analogy between those elements the equivalents of which may be mutually substituted for each other. We find, accordingly, in all other relations an analogy between potassium, sodium, and ammonium, on the one hand, and between aluminum, iron, chromium, and manganese on the other. In the group first mentioned, that of the chlorides, bromides, and iodides of certain metals, we find the same analogy between potassium, sodium, and ammonium on the one side, and between chlorine, bromine, and iodine on the other.

Now to these groups of analogous elements, the name of isomorphous groups has been given, as there is every reason to believe that, as elements, they possess the same form (ισος, equal, and μορφη, form); and the phenomena of identical form in compounds of different but analogous composition, have received the name of isomorphism. Two elements are isomorphous, which either crystallise in the same form, or may be substituted for each other in their compounds, equivalent for equivalent, (the other elements remaining unchanged) without affecting the form of the compound.

The doctrine of isomorphism enables us, in many cases, to decide on the formula of a compound, and, consequently, on its equivalent. Thus, we have seen that aluminum or iron may be replaced by chromium, without change of form, in alum; and we find that sesquioxide of aluminum, sesquioxide of iron, and oxide of chromium, also crystallise in the same form. Now, the composition of oxide of chromium was formerly uncertain; but, finding as we do that it is isomorphous with the other two sesquioxides, we conclude that it is also a sesquioxide, and that its formula is $Cr_2\,O_3$.

Again, chromic acid is found to contain twice as much oxygen for the same amount of chromium, or it may be represented as $Cr_2\,O_6$. This being a most improbable formula, we observe next, that chromic acid may be substituted for sulphuric acid, without change of form; in other words, these acids are isomorphous. But the formula of sulphuric acid is $S\,O_3$, and we, therefore, conclude, that the formula of chromic acid is $Cr\,O_3$; which agrees perfectly with the first observation, that it contains twice as much oxygen for the same weight of chromium as the oxide does; for $Cr\,O_3$ is the very same proportion as $Cr_2\,O_6$.

The following isomorphous groups have been established, and the existence of more is highly probable:—

1.

Silver	Ag
Gold	Au

2.

Arsenious Acid (in its unusual form)	$As_2\,O_3$
Sesquioxide of Antimony	$Sb_2\,O_3$

3.

Alumina	$Al_2\,O_3$
Sesquioxide of iron	$Fe_2\,O_3$
„ chromium	$Cr_2\,O_3$
„ manganese	$Mn_2\,O_3$

4.

Phosphoric acid	$P_2\,O_5$
Arsenic acid	$As_2\,O_5$

5.

Sulphuric acid	$S\,O_3$
Selenic acid	$Se\,O_3$
Chromic acid	$Cr\,O_3$
Manganic acid	$Mn\,O_3$

6.

Hypermanganic acid	$Mn_2\,O_7$
Hyperchloric acid	$Cl\,O_7$

7.

Salts of potash	KO
Salts of oxide of ammonium	AmO
(Or ammonia NH_3 + water, $HO = NH_4O$)	

8.

Oxide of silver	AgO
Oxide of sodium	NaO

9.

Baryta	BaO
Strontia	SrO
Lime (in arragonite)	CaO
Oxide of lead	PbO

10.

Lime (in Iceland spar)	CaO
Magnesia	MgO
Protoxide of iron	FeO
„ manganese	MnO
„ zinc	ZnO
„ cobalt	CoO
„ nickel	NiO
„ copper	CuO
„ lead (in plumbo calcite)	PbO

The above groups are almost all formed of compounds; either because these compounds are found to be actually isomorphous when themselves crystallised, as, for example, the sesquioxides in group 3; or because they may be mutually substituted for each other, in those compounds into which they enter, without change of form. This, as we have seen, is the case with the sesquioxides in the alums; and, indeed, three of these oxides have been obtained in crystals, and found to be themselves isomorphous. But it is also the case with the acids; for example, in groups 4 and 5, although we do not positively know, what is, however, most probable, that these acids possess, in each group respectively, the same form. Although, for example, we cannot say that arsenic and phosphoric acids are themselves isomorphous, since they do not crystallise, yet their salts are strictly isomorphous; and the analogy extends not only to form, but to colour, taste, and many other external qualities. So strong, indeed, is this external resemblance that, in many cases, we must actually decompose one of these salts, and ascertain whether it contain arsenic or phosphorus, before we can say whether the salt is an arseniate or a phosphate. The same extraordinary similarity in all external characters, is seen in the salts of the sulphuric and selenic acids.

We can hardly doubt that not only the salts, but the acids, are really isomorphous, and would be found so, if we could obtain them all in crystals; and we have the same reason to conclude that the elements of these acids are also isomorphous; that arsenic and phosphorus, sulphur and selenium, for example, crystallise in the same form.

Indeed, the only plausible explanation of the existence of isomorphous groups of compounds is, that the elements characterising those groups are isomorphous, and that hence their analogous compounds are so. If we assume that arsenic and phosphorus are isomorphous, then we see that $As_2 O_5$ must be isomorphous with $P_2 O_5$, since the oxygen in both is, of course, the same. In like manner, arseniate of soda, $As_2 O_5$, 2 Na O, HO, 24 aq., must be isomorphous with phosphate of soda, $P_2 O_5$, 2NaO, HO, 24 aq., since all the elements in these two salts are the same in nature, number, and arrangement, except that As_2 in the first is replaced by P_2 in the second, and the elements As and P have been assumed to possess the same form.

There is one case which requires explanation. It is the isomorphism of potash, KO, and oxide of ammonium $NH_4 O$; or, in other words, ammonia with 1 at: water, NH_3 HO. Here we have a body composed of 6 equivalents isomorphous with one containing only two. But, on the one hand, there is good reason to believe that the compound metal, ammonium, NH_4 exists; and if we represent this by a single symbol Am, its oxide will be Am O, corresponding in constitution to KO, each being formed of 1 eq. metal, and 1 eq. oxygen. It is true, Am is a compound; but, on the other hand, this compound acts as an element, and $Am = NH_4$ is only 1 eq. *of metal.* Besides, we cannot be certain that even potassium, K, is not also a compound, although we have not as yet succeeded in decomposing it, if it be one. At all events, it is a fact, that NH_4 may be substituted for K without affecting the form of the compound in which the substitution is made, as in the alums; and we have only to assume that the compound NH_4 happens to be isomorphous with the simple substance K, and all the facts would follow.

We shall have occasion to return to the subject of isomorphism, when treating of salts generally, and of their crystallisation.

Isomerism.

We have seen that, as a general rule, analogy of composition implies analogy or similarity in form and external properties. But it has been observed in a number of cases, that two or more compounds, formed of the same elements, in the same relative proportions, and having, therefore, the same composition in 100 parts, are yet entirely distinct from each other in all their properties. Such bodies are called isomeric bodies (from ισο equal, and μερος, part.)

It is obvious that, as the proportions of the elements are the same, the source of the difference in properties must be sought for in the *absolute number*, or in the *arrangement* of the atoms. Thus, acetic ether and aldehyde are two entirely different liquids, containing exactly the same relative proportions of carbon, hydrogen, and oxygen. These proportions, reduced to the smallest number of atoms, are $C_2 H_2 O$. Now, there is no doubt that the absolute numbers in aldehyde are $C_4 H_4 O_2$; and there is also no doubt that the absolute number of equivalents in acetic ether is $C_8 H_8 O_4$. Here it is evident that, although the proportions are the same, the equivalent of acetic ether is twice as large as the equivalent of aldehyde. Again, the composition, in 100 parts, and consequently the relative proportions of the elements, of urea is exactly the same as in hydrated cyanate of ammonia; while the equivalent of both compounds appears to be the same, or, in other words, they contain the same absolute number of atoms of the element. But we know that the hydrated cyanate of ammonia is represented by $NH_3+C_2 NO, HO$; and that urea contains neither ammonia NH_3, nor cyanic acid $C_2 NO$. Let us suppose the atoms in urea to be simply united thus, $C_2N_2H_4O_2$, and we see at once that the same relative and absolute number of atoms may readily give rise to perfectly distinct compounds. In some cases, we know what the arrangement is in both compounds. Thus, hydrated acetic acid, $C_4H_3O_3$, HO, and formiate of oxide of methule, $C_2H_4O+C_2HO_3$, both contain $C_4H_4O_4$. Such isomeric compounds are called *metameric;* and where the absolute number of atoms differs, *polymeric;* where the absolute number in one or both is unknown, they are called simply *isomeric.*

It is easy to see that, wherever the atoms of the elements of a compound admit of more than one arrangement, metameric compounds may occur. In binary compounds, such as water, HO, there is but one arrangement possible, as long as the absolute number of atoms is not doubled, trebled, or still further multiplied. But in such a compound as peroxide of iron, Fe_2O_3, for example, the elements might yield several metameric compounds, such as $2FeO+O$, $FeO+FeO_2$, $Fe+FeO_3$, not to mention the multitude of compounds which might be formed with precisely the same composition in 100 parts, by increasing the absolute number of atoms.

The discovery of isomerism, however unexpected, is thus entirely consistent with the atomic theory, of which it is merely a special case. Isomerism is of very frequent occurrence among organic compounds, owing, no doubt, to their usually large atomic weights, since the numerous atoms of the elements afford much scope for isomeric modifications; and doubtless this principle plays an important part in the processes of organic life and growth, as well as in decay.

Having premised the preceding general or introductory remarks, we now proceed to the actual description of the elements, and of their compounds, which constitutes Chemistry, properly so called.

It is not possible, in the present state of our knowledge, to follow any arrangement that shall not be open to objection. The different classes or groups of elements are not so clearly characterised as to permit us to follow a strictly scientific arrangement, and therefore we shall only adhere to the division of the elements into metalloids and metals; and, beginning with the former, describe the elements in the order of their importance and interest. It has already been stated that even this division is not always fully observable, since selenium is classed by some as a metal, and arsenic by others as a metalloid.

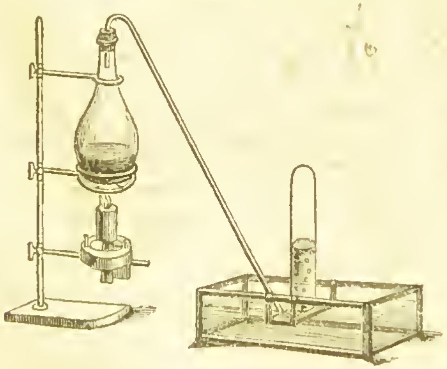
METALLOIDS.

There can be no hesitation as to that element which, being the most important of all, ought to be first treated. We therefore proceed to describe—

1. Oxygen. $O = 8.013$.

which is of all elements the most abundant; forms 89 p. c. by weight of all the water, and 23 p. c. of the atmospheric air of our globe; exists in all rocks, except rock salt; and is an essential element in all animal or vegetable bodies. It constitutes at least $\frac{1}{3}$ of the weight of our earth.

Obtained most easily by applying a heat rather below redness to a mixture of chlorate of potash with $\frac{1}{5}$ of its weight of peroxide of manganese. The latter undergoes no change, but promotes in a high degree the decomposition of the chlorate. The mixture being introduced into a small retort, or a small flask with a bent tube, may be heated by a spirit lamp, and the gas, which comes off very abundantly and rapidly, collected, over water, in the pneumatic



trough. The chemical change caused in the chlorate by heat is represented as follows:

$$KO, Cl\,O_5 = KCl + O_6$$

That is, 1 eq. of the salt yields 1 eq. chloride of potassium, KCl, which remains in the retort, and 6 eq. of oxygen, which escapes in the form of gas.

Properties.—A gas, colourless, tasteless, inodorous. Specific gravity (air=1·000) 1·1026, or, according to Thomson, 1·1111. A burning body, as a match of wood or paper, burns in the gas with greatly increased brilliancy; a spark on a piece of wood bursts out into flame. Iron wire burns in it, when heated white hot, with beautiful sparks. Phosphorus burns in it with an intense dazzling white light, &c.

Oxygen combines with all the other elements (except perhaps fluorine), and with most of them in several proportions. The combustion of bodies in oxygen is nothing but their combination with that element; the process, from the energy of the affinities, being attended with heat and light. Thus, when iron burns in oxygen, it yields oxide of iron, $Fe\,O$; and when phosphorus burns in oxygen, it produces phosphoric acid, P_2O_5. In all such cases, the oxygen and the combustible body disappear, and a new compound results.

Combustion, or the combination of a combustible with oxygen, goes on in atmospheric air, but much less rapidly and vividly than in pure oxygen, because, in air, the oxygen is diluted with four times its bulk of nitrogen.

Many substances slowly combine with oxygen without the development of heat or light; as, for example, iron, when it rusts.

In every case the combustible is said to be oxidised, or to undergo oxidation, and the compound formed is termed an oxide.

The whole structure of modern Chemistry is founded on the above simple theory of combustion, first proposed by Lavoisier; who, by using the balance, discovered that the burning body became heavier during the process, and could not, therefore, according to the then prevalent theory, have lost phlogiston (an imaginary element), or anything else.

Lavoisier having observed that all the acids then known were compounds of oxygen with combustible bodies, concluded that acidity depended on the presence of oxygen, and named that element accordingly (from οξυς, acid, and γενναω, to produce). The name is still retained, although we are now acquainted with many acids which contain no oxygen; and although, according to views now considered probable, hydrogen has more claim to the title of the producer of acids than oxygen. Besides, oxygen is now known to be an essential ingredient in bases, the basic power of which really seems to be in a close relation to their amount of oxygen. But the inconvenience of changing the name would be very great, so that, while many of the views of Lavoisier have been abandoned, his names are retained.

Lavoisier, among other views, held that combustion could not take place without the presence of oxygen. But subsequent experience has shown that although all combustions in our atmosphere, or in oxygen gas, depend on the presence of oxygen; the phenomenon of combustion is nothing more or less than chemical combination, attended by heat and light. Many examples might be adduced of combustion without oxygen; take, for example, the case of iron and sulphur, which, when heated, combine with much heat and light; or that of phosphorus, which, when introduced into chlorine, takes fire and burns, combining with the gas. Although, therefore, oxygen is concerned in all ordinary combustions, that is, in all which take place in our atmosphere, the student must bear in mind the true definition of combustion;—namely, "chemical combination, attended with heat and light."

Oxygen has been termed a supporter of combustion, as distinguished from a combustible body, such as phosphorus. But we are not to suppose that the oxygen has any greater, or any other share in combustion, than the phosphorus. It so happens, that the oxygen is a gas, and the phosphorus a solid. The heat and light, therefore, appear to proceed from the phosphorus; because the combustion can only take place where the two bodies are in contact. But, in reality, both bodies are equally concerned in the production of the heat and light; and while we may call phosphorus a supporter of combustion as well as oxygen, we may call oxygen a combustible as well as phosphorus.

In all combustions in our atmosphere, the heat and light, as above explained, although derived equally from both bodies, or rather, from the process of combination, appear to proceed from what is usually called the combustible, or burning body. But this is merely appearance; for while a jet of hydrogen, set fire to in a jar of oxygen, seems to burn and to give out the heat and light, a jet of oxygen in a jar of hydrogen may be set fire to and will then appear, as the hydrogen did before, to be the source of the heat and light, which in both cases was derived from the combination of oxygen with hydrogen.

Oxygen is necessary to the respiration of animals; but for this purpose pure oxygen is not fitted; and it has, therefore, in our atmosphere been diluted with four times its volume of another gas.

When a large quantity of oxygen gas is required, it is generally prepared by heating to redness, in an iron bottle, the peroxide of manganese, of which 88 parts yield 8 of oxygen, according to the equation $2MnO_2 = Mn_2O_3 + O$. Oxygen may also be obtained by the action of heat on nitrate of potash or nitre, on red oxide of mercury, or on red oxide of lead. In practice, the chlorate of potash (of which 124 parts yield 48 of very pure oxygen), although rather a dear salt, and the peroxide of manganese, which, although not very productive, is very cheap, are alone employed. On the small scale, the peroxide of manganese, heated with sulphuric acid, yields twice as much oxygen as when heated *per se*, according to the equation:

$$MnO_2 + SO_3 = MnO, SO_3 + O.$$

The sulphate of protoxide of manganese, MnO, SO_3, remains in the retort. This process is troublesome, and the retort is generally broken during cooling. A better process, lately proposed, is to heat bichromate of potash with an excess of sulphuric acid.

Since oxygen unites with all the other elements, and forms very numerous and important compounds, it may be well here to mention the principal classes of oxidised bodies, or oxides, as the compounds of oxygen are called.

The most numerous class of oxides is that of the basic oxides or bases. These are formed, in every case, by the union of a metal with oxygen. The most frequent formula for a basic oxide is MO (M representing 1 eq. of a metal). Examples, potash, KO, lime, CaO, protoxide of iron FeO, protoxide of manganese, MnO. Such bases are called protoxides. Next to these in importance are the sesquioxides, the formula of which is M_2O_3. Examples, sesquioxide of iron Fe_2O_3, sesquioxide of manganese, Mn_2O_3, sesquioxide of antimony, Sb_2O_3. Sesquioxides are in all cases weaker bases than the protoxides of the same metals; and, generally speaking, they are found to be weaker bases than protoxides. There are a very few basic oxides of the formula MO_2. Example, deutoxide or binoxide of tin SnO_2. Finally, there are also a very few basic oxides of the formula M_2O. Example, suboxide of copper, $Cu_2 O$. Both these last kinds of bases are very feeble, compared to the preceding kinds.

The next important class of oxides is that of the oxygen acids. These are most frequently composed of metalloids united to oxygen; but there are also oxygen acids formed of metals united to oxygen. Examples of the former, carbonic acid CO_2, sulphuric acid $S O_3$, phosphorous acid $P_2 O_3$, phosphoric acid $P_2 O_5$, nitric acid $N O_5$, hyperchloric acid $Cl O_7$: of the latter, arsenious acid $As_2 O_3$, antimonious acid $Sb_2 O_4$, antimonic acid $Sb_2 O_5$, chromic acid $Cr O_3$, manganic acid $Mn O_3$, hypermanganic acid $Mn_2 O_7$. It will be observed, that the formulæ of acids are very various; and it will also be noticed that where a metal forms an acid with oxygen, that acid contains more oxygen than the basic oxide or oxides of the same metal. Thus, sesquioxide of antimony which is basic, is $Sb_2 O_3$, while antimony forms two acids, one $Sb O_2$, or $Sb_2 O_4$, and the other $Sb_2 O_5$.

The third class of oxides is that of the neutral or indifferent oxides. These are neither decidedly acid, nor decidedly basic, and some of them play both parts; on the one hand combining with bases, as a weak acid would do; on the other, uniting with acids like a weak base. This is the case with water $H O$, which, itself neutral, combines both with acids and bases, forming compounds which are still acid or basic, and are called hydrates. Examples, $H O, S O_3$, oil of vitriol, or hydrated sulphuric acid; $K O, H O$, caustic potash, or hydrate of potash. Others do not enter into any combination, but are strictly indifferent; such as deutoxide of hydrogen, $H O_2$, and deutoxide (binoxide, peroxide, or superoxide) of manganese. Where, as in this last example, the metal also forms a basic oxide, or oxides, and an acid or acids, it is important to notice, that the indifferent oxide is intermediate in composition, as if a certain proportion of oxygen communicated basic properties, a somewhat larger proportion destroyed these without producing acidity, and a still larger share of oxygen gave to the compound distinctly acid characters. By inspecting the compounds of manganese with oxygen, we further see that of the two basic oxides, both of which contain less oxygen than the indifferent oxide, or superoxide, that which contains the most oxygen is the weaker base.

$Mn\ O$	Protoxide of manganese.	A powerful base.
$Mn_2\ O_3$	Sesquioxide of do.	A feeble base.
$Mn\ O_2$	Superoxide of do.	Neither basic nor acid.
$Mn\ O_3$	Manganic acid.	A strong acid.
$Mn_2\ O_7$	Hypermanganic acid.	A strong acid.

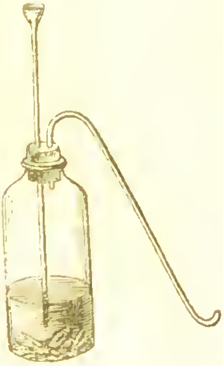
When the superoxide, or indifferent oxide of a metal, is acted on by an acid it loses oxygen, while a basic oxide, being left, combines with the acid; as in the process for obtaining oxygen by the action of sulphuric acid on peroxide of manganese, given and explained at p. 47.

Oxygen was discovered by Priestley, in 1774; and in the following year by the Swedish chemist, Scheele, without any knowledge of Priestley's discovery. The time, in fact, had come when Chemistry was studied in the true scientific spirit; and had these illustrious men not then discovered oxygen, it must, nevertheless, have been very soon discovered by some one else.

2. Hydrogen. H = 1.

Occurs in nature only in combination, chiefly in the form of water, of which it constitutes 11 per cent. by weight. It is an essential ingredient in all organised bodies.

It may be easily prepared by causing diluted sulphuric or hydrochloric acid to act on iron filings, or on granulated zinc. The best apparatus for the purpose is a wide-mouthed bottle, furnished with a closely-fitting cork. In this cork are made two holes, into one of which a tube properly bent is closely fitted, while into the other is inserted, also air-tight, a straight tube, reaching to the bottom of the bottle, and widened at its upper end, so as to form a funnel. Both tubes are open at both ends, and the bent tube terminates, within the bottle, just below the cork, while its further end dips under water in the pneumatic trough.



The metal being introduced into the bottle, and covered to the depth of an inch with water, the cork with the tubes is fitted in: the acid is poured in through the straight tube, and the bottle shaken, so as to mix the acid and water thoroughly. Enough of acid should be added to cause a brisk, but not violent effervescence; and as the end of the straight tube is covered by the liquid, the gas produced can only escape through the bent tube. Care must be taken not to collect the gas for use until the whole of the air originally in the upper part of the bottle has been expelled; otherwise the application of a light might cause a dangerous explosion. Perhaps the safest way is to collect, in a large jar full of water, as much of the gas which first escapes as would suffice to fill the gas-bottle twice, and to throw this away: what comes subsequently is pure. When the current of gas slackens, the addition of a little more acid, through the straight tube, causes it again to go on as briskly as at first.

When zinc and hydrochloric acid are employed, the process is represented by the following equation: $Zn + H\,Cl = H + Zn\,Cl$. That is, the zinc takes the chlorine of the acid, forming chloride of zinc, and the hydrogen is separated. When iron and sulphuric acid are used, the process is expressed by the equation $Fe + HO, SO_3 = H + Fe\,O, SO_3$. Here the hydrogen is supposed to proceed from water, the oxygen of which forms, with the iron, protoxide of iron, which again unites with the sulphuric acid, forming sulphate of protoxide of iron. It is to be observed, that this, the generally received explanation of the latter process, is very different from that of the former, although the phenomena in both are the same, namely, the escape of hydrogen and the formation of a neutral salt. When treating of acids and salts, we shall see how it is possible to do away with this complexity, and to bring both processes under one formula.

(The above simple method of obtaining hydrogen gas is equally applicable in all cases where a gas is to be produced by the action of an acid on a solid body, without the aid of heat; as in the cases of deutoxide of nitrogen, sulphuretted hydrogen, carbonic acid, &c. It has, therefore, been described minutely, and will hereafter be referred to in describing the preparation of the above gases.)

Properties.—Hydrogen is a gas, colourless, tasteless, and, when quite pure, devoid of smell. When prepared from common zinc or iron, it contains some foreign body, which gives it an unpleasant smell. It is the lightest body known, its Sp. G. being 0.0694 (Air = 1), or 16 times less than that of oxygen. A lighted candle, introduced into hydrogen, is extinguished, but the hydrogen takes fire at the mouth of the vessel, where it is in contact with the oxygen of the air, and burns rapidly away, giving out but little light, with an intense heat, and producing water, which, by proper means, may be condensed and collected. Hydrogen gas is not absorbed by water.

Hydrogen does not combine so readily with other bodies as oxygen does. It may be made, however, to combine with most of the metalloids and with a few of the metals. With chlorine, bromine, iodine, and fluorine, it forms powerful acids, the general formula of which is $H\,R$;* with carbon, sulphur, phosphorus, selenium, tellurium, and arsenic, it forms combustible gases, several of which have acid properties. With nitrogen it forms ammonia, NH_3, and probably two other compounds, ammonium, NH_4, and amidogen, NH_2.

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* R here stands for 1 eq. of any of the metalloids just mentioned.

From its extreme lightness, 100 cubic inches weighing only about 2·5 grs., while common air is about 14 times heavier, hydrogen is used for filling balloons.

Besides the processes above described, hydrogen is obtained by passing the vapour of water (steam) over red hot iron wire, when the iron is oxidised at the expense of the water; also by placing potassium or sodium in water, when these metals are instantly oxidised; and by heating to redness a mixture of potash, or soda, and organic matter, such as sugar, sawdust, &c.

HYDROGEN AND OXYGEN.

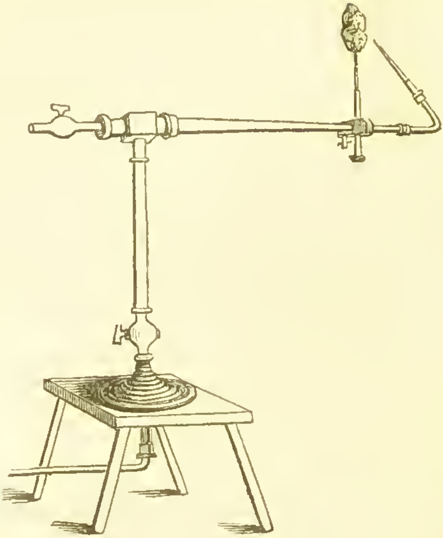
a. Water. $HO = 9{\cdot}013$.

Hydrogen may readily be made to unite with oxygen, whether pure or in the form of atmospheric air. When hydrogen is mixed with oxygen or with air, the mixture takes fire and explodes violently on the approach of a flame, or when the electric spark is passed through it. A jet of hydrogen, issuing from a tube, may be set fire to by the same means; and in both cases, water is the only product.

We have already seen that 1 grain of hydrogen combines with 8 of oxygen to form water; and as no other element takes up so large a proportion of oxygen, this is probably the reason why the combination of hydrogen with oxygen is attended with so intense a heat.

If hydrogen and oxygen be mixed in the exact proportion of 2 vol. of the former to 1 vol. of the latter, and the mixture set fire to, as it issues from a small tube, the most intense heat is produced that it is possible to obtain by combustion. The flame of the oxy-hydrogen blowpipe, as it is called, readily melts platinum and pipe-clay, substances which resist the fire of the hottest furnaces. By this means, Mr. A. Kemp has melted 6 oz. of platinum at once.

The gases, if previously mixed, should be made to pass through a safety-apparatus before being set fire to; but, as accidents have occurred even when the safety-apparatus was used, it is, in all cases, better to keep the gases in separate gas-holders, and to allow them to mix only in the tube, just before they are ignited, regulating the flow of the two gases so as to obtain the most intense heat. Any excess of either gas cools the flame and diminishes the effect. For the jet best adapted to this experiment, see the cut.



When a portion of spongy platinum, or of the finely-divided black powder of that metal, is introduced into a mixture of hydrogen with oxygen, or with air, the platinum soon becomes red-hot, and then the explosion instantly follows. Or if a jet of hydrogen be thrown on the metal in the air, it becomes red-hot and ignites the jet. On this principle is constructed the beautiful instantaneous light apparatus of Döbereiner.

It would appear that the platinum possesses the property of causing hydrogen and oxygen to combine on its surface, whereby heat is developed sufficient to make the metal red-hot; and it then acts as any other red-hot body, such as flame, would do, in causing the explosion.

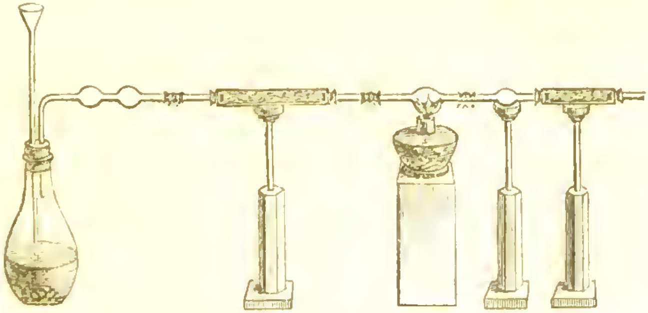
The observations of Döbereiner on the properties of the black powder of platinum may assist us to explain this singular property of platinum. He found that the powder condensed within its pores 253 times its volume of oxygen, and as the pores occupy only $\frac{1}{4}$ of the bulk of the powder, this oxygen must be in a state of condensation such that it occupies only $\frac{1}{1000}$ of its volume in the form of gas. In this state it must be denser than water, and we may easily conceive how it is thus rendered capable of at once combining with hydrogen. Spongy platinum only differs from the powder in being less minutely divided.

If a jet of hydrogen be set fire to and a cold dry bell jar held over the flame, the inside of the jar will instantly be covered with a film of dew, which rapidly increases, and at last condenses into drops of water. This water, if collected, is found to be quite pure; and if a known weight of hydrogen be burned, and the whole water collected without loss, the weight of the water will be 9 times that of the hydrogen ; the difference, or 8 parts in 9 of water, is oxygen.

This most important point, namely, the true composition of water, may be ascertained in other ways. Thus, if two vols. of pure hydrogen and 1 vol. of pure oxygen be mixed and confined over water or mercury, and if the electric spark be passed through the mixture, both gases will entirely disappear, and water alone will be the product. If the experiment be made in a graduated tube, and if, for example, 210 vols. of hydrogen be mixed with 100 vols. of oxygen, and the mixture exploded, 10 vols. of hydrogen will remain unchanged ; or if the proportions had been 200 vols. of hydrogen to 110 of oxygen, 10 of oxygen would have been left. Now, as hydrogen is 16 times lighter than an equal bulk of oxygen, it follows that 2 vols. of hydrogen must be 8 times lighter than 1 vol. of oxygen ; and thus we arrive at the same result as to weights as we obtain by burning hydrogen and weighing the water produced.

Another, and a very beautiful method, of ascertaining the composition of water, by weight, is the following :—

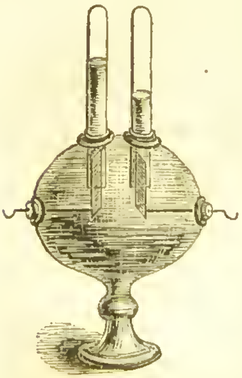
Into the bulb blown in the middle of a wide tube of Bohemian glass, the weight of which is known, there is introduced a weighed portion of oxide of copper. One end of the tube is then connected with an apparatus, from which a steady current of dry hydrogen is disengaged ; and to the other end is attached a tube containing fragments of chloride of calcium, a substance possessing a strong attraction for water ; this tube with its contents being also weighed. As soon as the whole of the atmospheric air of the apparatus has been entirely displaced by the hydrogen gas, heat is applied, by means of a spirit lamp, to the oxide of copper. Aided by the high temperature the hydrogen



very soon begins to decompose the oxide of copper, combining with its oxygen to form water; and before long the black colour of the oxide is changed to the red of metallic copper. The water which is formed condenses in the cold part of the tube beyond the bulb, but by heating that part of the tube the whole of the water is soon carried by the current of gas into the tube with chloride of calcium, where it is retained. The apparatus is now allowed to cool, and when the tubes have again become full of atmospheric air, they are weighed. That with the copper will be found lighter than before, the other heavier. The loss of the former is oxygen, the increase of the latter is the water which that oxygen has yielded, and, of course, the difference between the two is the hydrogen of the water.

Let us suppose the first tube, when empty, to have weighed 500 grs. and when filled with the oxide of copper 540 grs., the oxide of copper must weigh 40 grs. The tube with chloride of calcium weighs, before the experiment, say 300 grs. Now, we should find, after the experiment, that the first tube now containing metallic copper, would weigh 532 grs. and the other tube 309 grs. the former having lost 8 grs. (oxygen,) while the latter has gained 9 grs. (water.) Hence, the 9 grs. of water contain 8 of oxygen, and, of course, 1 grain of hydrogen. Moreover, this experiment tells us that 40 grs. of oxide of copper are composed of 32 of copper and 8 of oxygen; thus proving the composition of water by synthesis, and that of oxide of copper by analysis.

There is still another method of demonstrating the composition of water: namely, the decomposition of that fluid by galvanic electricity. When the electric current of a powerful battery is made to pass through water in an apparatus so contrived, that the gas given off at each pole may be received into a separate graduated tube, it is found that by the time the tube at the positive pole is half full, the tube at the negative pole is quite full; and on examination, the gas in the latter is found to be pure hydrogen, while that in the former is pure oxygen; and the proportion, by volume, is obviously 2 of hydrogen to 1 of oxygen, and from this, by means of the specific gravities of the gases, we obtain, as before, the proportion, by weight, of 1 to 8.



Water, which is thus proved to contain 1 eq. of hydrogen to

1 eq. of oxygen, represented by $H\,O$, is, at ordinary temperatures, a liquid, colourless, tasteless, and inodorous. It assumes the solid form, that of *ice* or *snow*, at 32° F., and all lower temperatures; and it takes the form of gas or vapour, that of *steam*, at 212° F., and retains that form at all higher temperatures. When ice is heated above 32°, it melts into water; and when steam is cooled below 212°, it condenses into water. Thus water possesses the liquid form only at temperatures lying between 32° and 212°.

Hence, in certain arctic regions, water is always, or nearly always, solid. Even in that state, however, and at all temperatures below 212°, it is always slowly assuming the gaseous form. It is in this way that watery vapour is constantly rising into the atmosphere from the surface of the sea, of lakes, of rivers, and of the soil; which watery vapour, being again condensed into the liquid form, falls back on the earth in the shape of rain or dew, or if frozen, as snow, hail, and hoar-frost.

Water is perfectly neutral; that is, it exhibits in itself neither acid nor basic properties: but it is capable of combining with both acids and bases, and indeed, seems to be almost essential to their activity. The compounds of water with acids and bases are called hydrates; as $H\,O, S\,O_3$, hydrated sulphuric acid, and $K\,O, H\,O$, hydrate of potash.

Water combines also with neutral salts, and that in two conditions. In one it is easily expelled by heat, and the salt, if crystallised, generally falls to powder when the water has been expelled. This is called water of crystallisation, and its quantity is often very large. In the other, a portion of water, generally 1 eq., is combined with the salt by so powerful an affinity that it is with some difficulty separated. This is called saline water, because it may be replaced by an equivalent of a neutral salt. In formulæ, water of crystallisation is represented by aq. (for aqua,) and saline water by $H\,O$. Thus, green vitriol is represented by $Fe\,O, S\,O_3 + H\,O + 6\,aq.$: that is, 1 eq. of neutral sulphate of protoxide of iron, 1 eq. of saline water, and 6 eq. of water of crystallisation. When this salt is gently heated, the 6 eq. of water of crystallisation are expelled, but the 1 eq. of saline water can only be expelled by a red-heat. It can also be replaced by a neutral sulphate, such as sulphate of potash, $K\,O, S\,O_3$, and the resulting double salt is $Fe\,O, S\,O_3 + K\,O, S\,O_3 + 6\,aq.$ Here, as in the green vitriol, the 6 eq. of water of crystallisation are easily expelled by a gentle heat.

In relation to acids, therefore, water acts the part of a base; in relation to bases, that of an acid; and in relation to neutral salts, that of a neutral or indifferent substance, or, indeed, of a neutral salt. Taking the three examples of hydrated sulphuric acid, HO, SO_3, hydrate of potash, KO, HO, and dry sulphate of iron, $Fe O, SO_3 + HO$, it is to be observed that the water in the first can only be replaced by a base, such as potash, KO, which would yield sulphate of potash, KO, SO_3; the water in the second can only be replaced by an acid, such as sulphuric acid, SO_3, which would yield the same salt, KO, SO_3; and the water in the third may be replaced by a neutral salt, such as sulphate of potash, KO, SO_3, which would give rise to the double salt, $Fe O, SO_3 + KO, SO_3$. Water in these three different characters is called basic water, hydratic water, and saline water, and, in addition to these, we have water of crystallisation.

Besides these numerous forms of combination, in which water most frequently loses the liquid form, it enters, as a liquid, into a peculiar kind of combination with the greater number of all known substances: it dissolves them. Of all liquids, water is the most powerful and general solvent, and on this important property its use depends. By the solvent power of water, substances, inert in the solid form, are made to assume the liquid form, and thus to become active—chemical action is promoted—substances mixed together may be separated from one another;—in short, without water, not only the operations of the chemist, but the processes of animal and vegetable life, would come to a stand.

The solvent power of water, in regard to solid bodies, is generally increased by heat. Hot water, therefore, dissolves more of most bodies than cold water does; so that when a hot saturated solution cools, it deposits a quantity of the dissolved solid, commonly in crystals.

Water readily dissolves or combines with, or absorbs, as it is termed, many gaseous bodies. The gas, in this case, assumes the liquid form; and, as heat tends to cause bodies to assume the gaseous form, it is obvious that heat must diminish, and cold increase, the solvent power of water for gases. Increased pressure also enables water to absorb more of a gas than it will do under the ordinary pressure, evidently because pressure favours the liquefaction of a gas, by forcing the particles nearer to each other.

In consequence of the great solvent power of water, it is never found pure in nature. Even in rain water, which is the purest, there are always traces of carbonic acid, ammonia, and sea salt. When the rain water has filtered through rocks and soils, and re-appears as spring or river water, it is always more or less charged with salts derived from the earth, such as sea salt, gypsum, and chalk. When the proportion of these is small, the water is called soft, when larger, it is called hard water. The former dissolves soap better, and is therefore preferred for washing; the latter is often pleasanter to drink, as its saline contents communicate to it a slight, but agreeable taste.

When water becomes so highly charged with foreign matters as to have an unpleasant taste, or to acquire medicinal virtues, it is called mineral water. Of mineral waters there are several kinds: those in which iron predominates are called chalybeate waters; where sulphur prevails, they are called sulphureous waters: acidulous waters are those which contain much free carbonic acid; and saline waters are such as contain neutral salts, generally sea salt, and sulphate of magnesia, or Epsom salt.

The only way to obtain perfectly pure water, is to distil it; and in the laboratory, no water except distilled water should ever be used, provided distilled water can be procured in sufficient quantity.

Water is the standard of specific gravity for liquid and solid bodies, and its specific gravity is therefore represented by 1.

b. Deutoxide of Hydrogen. $HO_2 = 17{\cdot}013$.

This compound is formed, in some cases, where oxygen is presented in the nascent state to water. The best process is that of Pelouze, which consists in adding to diluted hydrofluoric acid (fluosilicic or phosphoric acids may equally be used), kept very cold, exactly so much of the peroxide of barium, that neither barium nor the acid can be detected in the liquid, the whole of both being precipitated as fluoride of barium: $BaO_2 + HF = BaF + HO_2$. The deutoxide of hydrogen is dissolved by the surrounding water, and the filtered liquid is concentrated by being placed under the exhausted receiver, along with a vessel containing sulphuric acid, the whole being kept cold. The process, even in this form, is tedious and difficult, but much less so than the original method of Thénard, who discovered the compound.

The deutoxide, peroxide, or superoxide of hydrogen, when as free from water as possible, is a syrupy liquid, colourless, and possessed of a slight disagreeable odour, like that of bleaching liquor, and of a peculiar nauseous, bitter, and astringent taste. Its Sp. G. is 1·453 (water = 1). It does not become solid, even in a very intense cold.

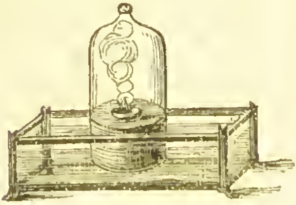
This compound is very easily decomposed, yielding water and oxygen. The contact of carbon, of many metals, and even of metallic oxides, also of many salts, causes the separation of oxygen, often with explosion, and sometimes with a flash of light. It is very remarkable that peroxide of manganese, for example, should cause this rapid decomposition, without combining with any part of the disengaged oxygen; and still more astonishing, that oxide of silver should decompose it with explosion, while the oxide of silver, so far from combining with more oxygen, loses all that it previously contained, and is reduced to the metallic state. We cannot, at present, explain these phenomena. The application of heat to the deutoxide of hydrogen, causes oxygen to escape with effervescence. It is less easily decomposed when diluted, and especially if acidulated; the presence of a base, on the contrary, hastens its decomposition.

It is very probable that this remarkable compound will be found to possess valuable properties as a medicinal agent, and it is much to be desired that its preparation could be rendered easier.

3. Nitrogen. N=14·19.

Syn. *Azote.*—Discovered by Rutherford, in 1772. Occurs principally in the atmosphere, of which it forms 79 or 80 parts in 100 by volume, and about 77 by weight; also, in minute quantity, in the atmosphere as ammonia. It is an essential ingredient of all animal tissues, and of all such vegetable products as can be converted into blood in the animal body; also of the vegetable bases, and other vegetable compounds, such as indigo, &c. &c.

It is best obtained by the action of burning phosphorus on a confined portion of air, over water. The phosphorus takes the oxygen, forming phosphoric acid, which is soon removed by the water, and nitrogen gas is left.



Nitrogen is a colourless and transparent gas, devoid of taste and smell, and chiefly distinguished by the absence of active properties. It does not support combustion, neither does it burn itself. It is incapable of supporting animal life, and consequently an animal, immersed in pure nitrogen, soon dies; but only because oxygen is absent, for nitrogen itself is so far from being poisonous, that the air we breathe contains $\frac{4}{5}$ths of its bulk of that gas in an uncombined state. It serves to dilute the oxygen, and for that purpose it is admirably adapted, from the absence of marked characters or strong affinities. Its specific gravity is rather less than that of air, being 0·976.

Nitrogen cannot be made to unite directly with any element, and only forms combinations when one or both elements are in the nascent state. It is, therefore, unlike the other metalloids, in a high degree chemically indifferent or neutral. But, under favourable circumstances, it does combine with most of the metalloids, and with several metals. Its most important compounds are those with oxygen and with hydrogen. Almost all compounds of nitrogen are easily decomposed, and many of them are even dangerous, from their tendency to explode from very slight causes.

It is this very character of easy decomposability that gives to the compounds of nitrogen their very high importance in the organised kingdoms of nature. We shall hereafter see how important a part these compounds perform in the formation, as well as in the destruction, of organic bodies.

NITROGEN AND OXYGEN.

a. Atmospheric Air.

The air of our atmosphere is formed of nitrogen and oxygen, not in a state of combination, but simply mixed together. Dalton has shown that, when any two gases, however different in density, are placed in communication, they are very soon found to be completely and equally mixed, even although they have no tendency to combine chemically. This is the case with the gases in air. The properties of each are present, only modified slightly by the presence of the other; whereas chemical combination gives rise to new compounds, possessing entirely new properties. This is eminently the case in the compounds which are really formed between nitrogen and oxygen, so that we are forced to look upon the air as a mixture merely.

It is remarkable, however, that the proportions of the gases are such as correspond almost exactly, by weight and by volume, to 2 eq. nitrogen and 1 eq. oxygen. Of 100 vol. of air, 79 or 80 are nitrogen, and 20 or 21 oxygen. Here we have the ratio of 4 vol. to 1. 100 parts of air, by weight, contain nearly 77 of nitrogen and 23 of oxygen; that is, almost exactly 28 of nitrogen to 8 of oxygen, or N_2O.

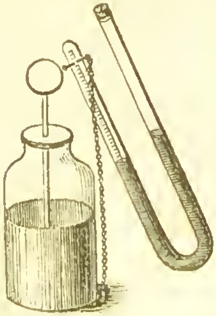
The physical properties of air are well known. It is, like all gases, elastic, and it possesses such a density, that 100 cubic inches weigh about 31 grs. Hence, the whole atmosphere presses on the surface of the earth with a very great force, equal to about 14 lbs. on each square inch of surface. In other words, a column of air, 1 square inch in base, and equal in height to the atmosphere, weighs 14 lbs. But the further consideration of this subject belongs to physics. Air is made the standard of specific gravity for gases and vapours, and its Sp. G. is made 1·000.

The chemical properties of air are chiefly those of the oxygen it contains, modified by the presence of 4 times its bulk of the negative body, nitrogen. Air supports combustion, and the respiration of animals, as long as the proportion of oxygen does not fall below a certain amount.

Besides nitrogen and oxygen, the air always contains more or less watery vapour, which is almost equally important to animal and vegetable life, since neither animals nor plants can live long in a perfectly dry air.

Air also contains, as ingredients essential to the life of plants, and thus indirectly also to that of animals, minute proportions of carbonic acid and of ammonia. The amount of the former seldom, in the open air, exceeds $\frac{1}{1000}$ part of the weight of the air; while the proportion of ammonia is much smaller even than this.

When it is required to ascertain the exact proportion of oxygen in any specimen of air, the object may be attained in a variety of ways. The operation is called eudiometry, and the instruments employed eudiometers. The most commonly employed is that of Volta, modified by Ure, which is simply a graduated glass tube, closed at one end, bent as in the figure, and furnished with two platinum wires, to allow the electric spark to pass. The air being introduced and measured, half its bulk of pure hydrogen gas, or thereabouts, is added, and the whole measured again. The gas being confined by water or mercury, and the open end of the tube stopped by the finger or thumb, the spark is passed through the mixture, when an explosion takes place, and a certain portion of the mixture disappears, the water or mercury rising in the tube to supply its place. The residue is now measured, and $\frac{1}{3}$ of the volume which has disappeared is oxygen. It is obvious that, if there be enough of hydrogen, the whole of the oxygen will assume the form of water, and both the oxygen and hydrogen of that water must lose the gaseous form.



Now, as water is formed of 2 vol. hydrogen to 1 vol. oxygen, $\frac{1}{3}$ of the volume of the gases which have combined must be oxygen.

If, for example, 100 measures of air are mixed with 50 of hydrogen, the bulk of the whole will be 150. If, now, after explosion, 87 parts remain, it is plain that 63 have disappeared, and of these 63 measures 21, or $\frac{1}{3}$, are oxygen, originally contained in the 100 of air, while 42, or $\frac{2}{3}$, are hydrogen.

Gay-Lussac has lately proposed to remove the oxygen from a measured portion of air by means of copper moistened by sulphuric or hydrochloric acid, which soon absorbs that gas completely. The diminution of volume here is exactly equal to the proportion of oxygen present.

There are many other eudiometrical methods, but the above are the best.

The amount of water in the atmosphere is ascertained by hygrometers, of which there are various kinds. That of Daniell is the best. It is founded on the fact, that the temperature at which the water contained in the air is deposited as moisture, varies with the amount of moisture present. The drier the air, the more must it be cooled before it begins to deposit moisture. If the air be saturated with moisture, the cooling of it one degree will cause a deposition of dew, and the temperature at which dew is deposited is called the dew-point. The details of this and other hygrometers belong to physics.

The presence of water in the atmosphere may be shown at any time by exposing a deliquescent substance, such as chloride of calcium, to the air, when it quickly becomes moist and finally liquefies by attracting moisture. Air, or any other gas, may thus be dried, either in a tube over mercury, into which the drying substance is introduced, or by passing the gas through a long tube filled with the substance in coarse powder, or through strong sulphuric acid, which has a powerful affinity for water.

The uses of atmospheric air are obvious. Besides supporting animal and vegetable life, it is essential to all our modes of obtaining heat and light by combustion.

It is very important to remark, that although the processes of respiration and combustion, as well as that of the decay and putrefaction of animal and vegetable matter, are constantly removing oxygen from the air, yet the proportion of that element never diminishes, being kept up by the process of vegetable life. In like manner, respiration and combustion are continually sending carbonic acid into the atmosphere in place of the oxygen they consume, and yet the air does not become more highly charged with carbonic acid; for the same process of vegetable life which restores oxygen to the air, removes an equal bulk of carbonic acid,—from which, indeed, the oxygen thus restored is derived.

b. Protoxide of Nitrogen. $NO = 22·203$.

Syn. *Nitrous Oxide; Intoxicating or Laughing Gas.*—Prepared by applying a moderate heat to pure nitrate of ammonia in a retort. The salt melts, boils, and is soon entirely volatilised in the form of water, which trickles down the neck of the retort, and protoxide of nitrogen, which being gaseous may be collected over water. The following equation represents the change:

$$(NH_3 + NO_5) = 3HO + 2NO.$$

Showing that 1 eq. of ammonia and 1 eq. of nitric acid yield 3 eq. water, and 2 eq. protoxide of nitrogen.

This compound is a gas, colourless and transparent. It has a faint smell and a sweetish taste. It is slowly absorbed by water, and therefore cannot be long kept over that liquid. Its specific gravity is 1·527. It may be liquefied by a pressure of 50 atmospheres.

By weight it contains 8 parts of oxygen to 14 of nitrogen, and by volume, 2 vol. of nitrogen and 1 vol. of oxygen, condensed into the bulk of 2 vol. Hence this gas contains its own bulk of nitrogen, and half its bulk of oxygen, while air only contains $\frac{1}{5}$ of its bulk of that gas. Consequently, as some combustible bodies, such as phosphorus, or a candle, if burning, are capable of decomposing this gas and seizing its oxygen, they burn in it with great brilliancy. Probably for a similar reason it is capable of supporting life for a short time, if respired, and its action on the human system is most remarkable. In most persons it causes very agreeable sensations, a sense of lightness, a rapid and brilliant flow of ideas, accompanied with an irresistible tendency to laughter and to very violent muscular exertion. These effects only last for a minute or two after tho gas has been breathed as long as possible: but they are not followed, like those of other excitants, by any sense of depression or languor: on the contrary, a certain feeling of exhilaration and unusual lightness of spirits is often felt for a whole day after. In some cases the effects are unpleasant, such as headache, a rush of blood to the head, and a tendency to stupor. The experiment must be therefore made with caution, and the gas withdrawn, should the face of the experimenter appear flushed to any considerable extent. As he is often, however, unwilling to relinquish the bag of gas, an aperture should be made in the side of the breathing-pipe, and stopped with a cork, which may be removed if necessary, thus admitting air to the mouth, and putting an end to all danger. These very singular properties of this gas were first discovered by Davy; and in a physiological point of view, they merit further investigation than they have yet received. The gas has been tried in medicine, but hitherto without much benefit: although in America it is said to have been found useful in cases of melancholia.

Protoxide of nitrogen is neutral or indifferent, and has hardly any tendency to combine with other bodies. According to Pelouze, however, it combines with the salts of sulphurous acid, or sulphites.

c. Deutoxide of Nitrogen. $NO_2 = 30{\cdot}216$.

SYN. *Nitric Oxide: Nitrous Gas.*—Best obtained by the action of copper clippings on moderately strong nitric acid, in the apparatus, p. 49. The metal is dissolved with effervescence, and the gas may be collected and preserved over water.

A gas, transparent and colourless. Its taste and smell are not known, because as soon as it comes in contact with air, it forms, with the oxygen, red vapours of nitrous acid, which have a suffocating smell and a rough, acid, corrosive taste. It supports, like the preceding gas, the combustion of burning phosphorus, and for the same reason, namely, that it contains half its bulk of oxygen, being formed of equal volumes of nitrogen and oxygen, united without condensation. Its specific gravity is consequently the mean between those of oxygen and nitrogen, or 1·0416. A burning candle is extinguished in this gas, and it not only does not support life, but cannot be breathed, as it forms nitrous acid gas in the mouth, and the glottis instinctively closes against the latter.

Its most distinctive character is that of forming, when mixed with air or oxygen, a red gas or vapour, which is nitrous acid, and which instantly disappears if in contact with water, being absorbed by that liquid. As the formula of the deutoxide is NO_2, and that of nitrous acid, NO_4, it is plain that the latter may be formed from the former by the mere addition of oxygen. As the red vapours are very remarkable, the deutoxide may be used as a test of the presence of free oxygen in a gaseous mixture.

If a few drops of bisulphuret of carbon be added to a jar of this gas, and a light applied to the mixture, it burns rapidly with a bright blue flash of light.

The deutoxide of nitrogen is abundantly absorbed by any solution containing a salt of protoxide of iron, such as green vitriol, forming a brown solution, from which the gas may be expelled unchanged by boiling. This solution absorbs oxygen, and has been used in eudiometry, but it does not give accurate results.

d. Hyponitrous Acid. $NO_3 = 38{\cdot}229$.

SYN. *Acide Nitreux ; Salpetrige Saüre.*—It is formed when a strong base, such as potash, is brought into contact with the preceding gas, protoxide of nitrogen being given off, while the acid unites with the base. Thus,

$$KO + 2NO_2 = KO, NO_3 + NO.$$

It is best obtained, however, by heating 1 part of starch in 8 parts of nitric acid, Sp. G. 1·25, and conducting the disengaged gases, first through a long tube filled with chloride of calcium, to remove water, and then through a dry tube cooled down to —4° F. in which latter the acid condenses, as a very volatile liquid which, while cold, is colourless, but at the ordinary temperature becomes green. Its properties are little known.

In contact with water it is destroyed, giving rise to nitric acid and deutoxide of nitrogen, thus :

$$3NO_3 = NO_5 + 2NO_2.$$

The salts of this acid are obtained by heating a nitrate,—for example, nitrate of potash or soda,—till it begins to precipitate nitrate of silver brown. The whole is then precipitated by nitrate of silver, the precipitate dissolved in boiling water, and the hyponitrite of silver crystallises on cooling. From this salt, by the action of soluble chlorides, the other hyponitrites may be obtained. They have been little studied.

e. Nitrous Acid. $NO_4 = 46{\cdot}242$.

SYN. *Acide Hyponitrique. Untersalpetersaüre.*—This is the acid which appears as red vapours when deutoxide of nitrogen mixes with air, or with oxygen. 1 vol. deutoxide of nitrogen, and ½ vol. of oxygen, if mixed quite dry, and cooled, form the liquid nitrous acid ; but it is most easily obtained by distilling dry nitrate of lead. Equation,

$$(PbO, NO_5) = PbO + O + NO_4.$$

In this experiment oxide of lead is left, and oxygen gas and nitrous acid pass over, the latter condensing in the well-cooled receiver. If intensely cold, it is colourless; but as it becomes warmer, it assumes a yellow or orange colour. Its

Sp. G. in the liquid form is 1·42 It boils at about 82°, and is converted into a deep red vapour, or gas, which, if further heated, becomes nearly black, or impervious to light. If once mixed with air or any other gas, it can only with very great difficulty be condensed, so that it is commonly seen in the form of vapour. It has an unpleasant suffocating smell, and cannot be breathed with impunity even for a moment. It supports the combustion of almost all combustible bodies, by virtue of its large proportion of oxygen.

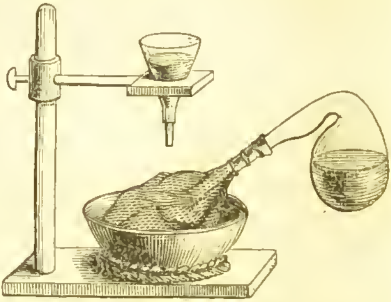
In contact with water, it is destroyed, giving rise, like the preceding acid, to nitric acid, and deutoxide of nitrogen. Thus, $3\ NO_4 = 2\ NO_5 + NO_2$. As it undergoes the same change in contact with all bases hitherto tried, its salts are unknown. Along with pure nitric acid, it forms the orange-fuming nitric acid of the shops, often called nitrous acid.

f. Nitric Acid. $NO_5 = 54{\cdot}255$.

Formula of the hydrated acid, HO, NO_5, or $H, NO_6 = 63{\cdot}268$.

This, the most important of all the compounds of nitrogen and oxygen, occurs very frequently in nature, chiefly combined with potash or soda, forming nitre and cubic nitre; also in minute proportion in rain-water after thunder-storms. It is formed in natural or artificial nitre beds, where animal or vegetable matter containing nitrogen is exposed to the air along with bases. The nitrogen being disengaged as ammonia, NH_3 is oxidised along with the hydrogen, yielding nitric acid and water; thus, $NH_3 + O_8 = NO_5 + 3\ HO$. The acid is seized by the base present, and nitre is formed. The nitric acid occasionally found in rain-water is also produced by the oxidation of ammonia; its quantity is too small to arise from the oxidation of the nitrogen of the air. The dry acid, NO_5 is unknown in the separate form; if we attempt to separate it from water or a base, it is resolved into nitrous acid and oxygen; thus, $NO_5 = NO_4 + O$.

The hydrated acid, HO, NO_5, or H, NO_6, is the substance commonly called nitric acid. It is best prepared by the distillation of a mixture of equal weights of hydrated sulphuric acid, or oil of vitriol, and of nitre or saltpetre, the nitrate of potash. The salt in coarse powder being introduced into a plain retort, the acid is poured in by means of a retort funnel. The retort is then placed in a sand-bath over the lamp, and cautiously heated, till the acid begins to drop into the receiver, which is to be surrounded with cold water. As the nitre generally contains a little sea-salt, the first portions of acid which distil are impure, containing chlorine, and nitrous acid; but they serve to wash quite clean the neck of the retort, on which some sulphuric acid is commonly to be found, in spite of all our care, as well as traces of the powdered nitre. It is best, therefore, to collect the first portion, say $\frac{1}{10}$ of the whole, in a separate receiver, and when the liquid that drops is found to be free from chlorine (by the test of nitrate of silver), the receiver is changed, and the rest of the nitric acid is thus obtained quite pure, or at most, slightly tinged by nitrous acid. By this simple device, we avoid the necessity of redistilling the acid, as commonly directed. The impure portion which first passes over, is extremely well adapted for all experiments of illustration, and ought to be carefully preserved for such purposes.



The following equation explains the change in this process:—

$$(KO, NO_5) + 2\,(HO, SO_3) = (KO, HO, 2\,SO_3) + HO, NO_5.$$

For 1 eq. of nitre, we take 2 eq. of oil of vitriol, and we obtain 1 eq. of hydrated bisulphate of potash, and 1 eq. of hydrated nitric acid. We take equal weights of the materials, because 1 eq. of nitre weighs 102, while 2 eq. of oil of vitriol weigh 98; and a slight excess of the latter is advantageous rather than otherwise. By using 1 eq. of oil of vitriol, we may also obtain nitric acid; but a much higher temperature is required, and a large part of the acid is decomposed into oxygen, which escapes, and nitrous acid, which combines with the nitric acid, giving it a deep red colour, and causing it to give out red fumes. Moreover, in the latter case, neutral sulphate of potash is left, which can hardly be got out of the retort without breaking it; while the bisulphate of potash, formed in the operation first described, may be easily dissolved out by hot water.

Hydrated nitric acid, when pure, is a colourless liquid, giving out dense gray fumes, on exposure to the air. Its Sp. G. is 1·52 to 1·53. It freezes at 40°, and boils at 108°. If diluted somewhat with water, so as to have the Sp. G. 1·42, it boils at 248°; but if still weaker, it boils more easily, and becomes stronger, till the boiling point reaches 248°, when it distils over unchanged. Nitric acid has a pungent, rather disagreeable smell, is very acid and corrosive, and stains the skin, and organic matter in general, yellow.

It has a strong attraction for water, and becomes hot when mixed with it. (Acid of middling strength, mixed with snow, causes it to liquefy instantly, producing intense cold.)

Nitric acid is very easily decomposed. If passed through a red-hot porcelain tube, it is resolved into oxygen and nitrogen. All combustible or oxidisable bodies deprive it of oxygen, reducing it to nitrous acid, hyponitrous acid, or deutoxide of nitrogen; and even, in some cases, removing all the oxygen, and leaving only nitrogen gas. The action is generally attended with heat; and in some cases, such as phosphorus and essential oils, combustion takes place, and even dangerous consequences may ensue from the acid, or the burning body; which is scattered about by the violent commotion. Nitric acid is, therefore, a very powerful oxidising agent, and is much used for oxidising and dissolving metals, such as silver, copper, mercury, &c. It is remarkable that the very strongest acid does not attack metals; but, on the addition of a few drops of water, a most violent action ensues.

The presence of nitric acid in a liquid is best ascertained by adding pure oil of vitriol, and then a drop or two of solution of green vitriol. If nitric acid be present, a red or brown colour will appear where the two liquids meet; and by this test $\frac{1}{21000}$ of nitric acid may be detected.

Pure nitric acid ought to be entirely volatile; and when diluted with distilled water, to give no precipitate with the salts of baryta, or of silver.

Nitric acid is used in medicine, and in the arts; in the latter, as aquafortis. To the chemist, it is one of the most valuable agents, and is daily employed as a means of oxidising metals and organic substances. The tendency of this acid to yield oxygen to combustible bodies is found also in its salts, especially at a red-heat; and hence, nitrate of potash, or saltpetre, is an essential ingredient of gunpowder, and of the various mixtures used for rockets and fireworks; in all of which it is mixed with charcoal and sulphur.

With bases, nitric acid forms salts called nitrates. Most of these are neutral, with the general formula MO, NO_5; but there are a few basic nitrates, in which one or more atoms of the base are added to the neutral salts. All the nitrates are decomposed by sulphuric acid, and they may be recognised by deflagrating with red-hot charcoal, and by the test above given for nitric acid, which distinguishes them from other deflagrating salts, such as chlorates, &c.

NITROGEN AND HYDROGEN.

a. Amide. $NH_2 = 16{\cdot}19$.

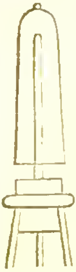
Syn. *Amidogen.*—This compound is unknown in a separate state, but is believed, with good reason, to exist in many compounds. If potassium, for example, be heated in dry ammoniacal gas, NH_3, $\frac{1}{3}$ of the hydrogen is expelled, and an olive-coloured solid remains, the composition of which is K, NH_2. It is viewed as a compound of potassium with amide, the amidide or amiduret of potassium. When put into water, potash and ammonia are formed, thus, $K, NH_2 + HO = KO + NH_3$. Compounds of amide with sodium, with carbonic oxide (oxamide), with benzoyle (benzamide), and other substances, are known. Their general character is, in contact with water, and under the influence of acids and bases, to be resolved into ammonia and an oxidised product, commonly an acid. Thus oxamide, $C_2 O_2, NH_2$, along with water, HO, in the presence of an acid or an alkali, yields ammonia, NH_3, and oxalic acid, $C_2 O_3$. It is this very powerful affinity for hydrogen which has hitherto defeated all our efforts to isolate amide. The various compounds of amide will be described in their proper order.

b. Ammonia. $NH_3 = 17{\cdot}19$.

Syn. *Volatile alkali*—Occurs in combination with hydrochloric acid, as sal ammoniac; in the urine of animals, especially of birds and reptiles, as urate of ammonia; in several aluminous and ferruginous rocks and earths in small quantity; finally, in the air, as a constant result of the putrefaction, decay, or combustion of organic matters containing nitrogen.

It is formed abundantly in putrid urine (from urea), and in the destructive distillation of organic nitrogenised matter, as, in Egypt, by heating camel's dung; in Europe, formerly, by distilling horn, hence the name spirit of hartshorn, at present by distilling any animal refuse; or in the distillation of coal in gasworks, which yield abundance of ammonia. In all these cases it is found as carbonate.

To obtain ammonia, powdered sal-ammoniac is mixed with about an equal weight of dry hydrate of lime (slacked lime), and the mixture heated in a retort, or a flask fitted with a bent tube. The ammoniacal gas is abundantly disengaged, and may be collected over mercury, or, as it is much lighter than air, by displacement, the tube being made to reach, as in the cut, to the closed end of the gas-receiver, the open end being downwards. A large tube or vessel may be easily filled with the gas in this way, and preserved by immersing the open end, when filled, in a small cup of mercury. The following equation represents the change in its production. $(NH_3, HCl) + (CaO, HO) = CaCl + 2\ HO + NH_3$.

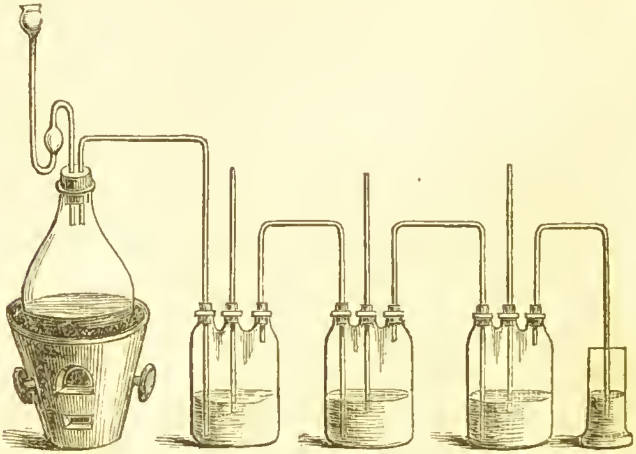


Ammonia is a gas, transparent and colourless, of a very pungent and peculiar smell and taste. It is liquefied by a pressure of about five atmospheres. It is instantly absorbed by water, forming the solution of the gas called aqua or liquor ammoniæ. It extinguishes a candle, does not burn itself under ordinary circumstances, and, if respired undiluted, is fatal to animal life. Its Sp. G. is 0.5902, being thus little more than one half as heavy as air. It possesses strongly alkaline or basic properties, neutralising the strongest acids. The approach of any gaseous or volatile acid, such as carbonic, hydrochloric, or nitric acids, to the mouth of a jar of ammonia, causes the formation of dense white clouds of carbonate, hydrochlorate, or nitrate of ammonia. By this property and by its smell, it is easily detected and recognised.

Ammonia is formed by the union of 3 vol. hydrogen and 1 vol. nitrogen, which yield not 4 vol. but 2 vol. ammoniacal gas. Here condensation to one half has taken place.

AQUA AMMONIÆ OR LIQUOR AMMONIÆ.

This most useful re-agent is best prepared by causing the gas disengaged from the above mixture of sal-ammoniac and slaked lime by heat, a little water having been previously added to moisten the powder, to pass through cold water in an apparatus, furnished with a safety-tube, to prevent undue absorption, the gas being washed by means of a very little water placed in an intermediate bottle. The water, if kept cold, will absorb about 670 times its bulk of the gas, by which it is increased in bulk, acquires a Sp. G. of only 0·872, and becomes possessed of all the chemical properties of the gas in a very high degree. This is the aqua ammoniæ fortissima of the manufacturers, and for medical use it requires to be diluted till it has the Sp. G. of 0·96. At 0.872, it becomes 32.5 per cent. of dry gas; at 0.96, hardly 10 per cent. Hence, by adding 8 vol. of water to 3 vol. of the strongest ammonia, we reduce it to the ordinary medical strength, which is also sufficiently strong for the usual chemical purposes.



This solution is constantly employed by the chemist for neutralising acids, and precipitating insoluble bases. It has the very great advantage of not introducing any fixed matter, so that the re-agent may be totally expelled by a red-heat. In medicine it is much employed, internally, as a diffusible stimulant, and externally as a powerful rubefacient, and also along with oil as a counter-irritant. If it can be procured in time, it is the best antidote to prussic acid.

With acids, ammonia forms salts, which are recognised by their yielding the pungent smell of ammonia when mixed with caustic potash or slacked lime. They are either volatile in the fire, as carbonate, sulphate, &c.; or they are decomposed, the ammonia being driven off and the acid remaining behind, as phosphate of ammonia. For the constitution of the salts of ammonia, see below.

c. Ammonium. $NH_4 = 18{\cdot}19$.

This compound, like amide, is not known in the separate state; but we have reason to believe that it exists, and has the chemical relations of a metal: hence its name.

When a salt of ammonia is decomposed by galvanic electricity, the negative pole terminating in a drop of mercury, the mercury swells to many times its original bulk, becomes almost solid, but retains its metallic aspect. The same compound is formed when an amalgam of mercury with potassium or sodium is placed in aqua ammoniæ, or in contact with a moistened ammoniacal salt. It is crystalline, and has been regarded as an amalgam of mercury and ammonium. When removed from the pole, and placed in water, it gives off ammonia and hydrogen, and the mercury resumes its original bulk. The remarkable circumstance is, that the amalgam contains so small a weight of ammonium (or of ammonia + hydrogen), although its properties are so different from those of the mercury. But, if we suppose an amalgam to be formed of 10 eq. of mercury and 1 eq. ammonium, this would contain less than 2 per cent. of the latter. There is, therefore, nothing unreasonable or very improbable, in the idea of a compound metal ammonium, NH_4. Indeed, if we assume its existence, we are enabled to take a view of the constitution of the salts of ammonia, which makes them analogous to those of the other alkalies.

It was formerly the universal opinion that ammonia, NH_3, combined directly with oxygen acids, such as sulphuric acid, SO_3, as well as with hydrogen acids, such as hydrochloric acid, HCl. According to our present knowledge, the hydrochlorate of ammonia does really contain the elements $NH_3 + HCl$, although we may suppose them otherwise arranged: but it has been shown that sulphuric acid, SO_3, although it can be made to unite with ammonia, does not produce sulphate of ammonia: but that the formation of this latter salt requires, besides the elements of ammonia and sulphuric acid, those of 1 eq. of water, HO; and that the salts of ammonia, with the oxygen acids in general, contain, as an essential ingredient, this 1 eq. of water. It is not easy to see why ammonia should form neutral salts without the aid of water, when acted on by hydrogen acids, and should require water when combining with oxygen acids. But if we admit that ammonium exists, and is the true basic radical in all these salts, the whole becomes clear. In that case, $NH_3 + HO$, ammonia + 1 eq. of water, becomes NH_4, O, or oxide of ammonium; sulphate of ammonia + water ($NH_3, HO + SO_3$) becomes dry sulphate of oxide of ammonium, $NH_4\,O, SO_3$; and hydrochlorate of ammonia, NH_3, HCl, becomes chloride of ammonium, NH_4, Cl. It has been observed, that the oxygen acid salts of ammonia + water are isomorphous with the dry salts of potash. Now, on the old view, we can trace no analogy between NH_3, HO, SO_3, and KO, SO_3; but, if we admit the existence of the metal ammonium, and, still more, if we represent it by the symbol Am. the analogy becomes obvious. Thus we have the two series—

	Potassium.	Ammonium.	Do. at full length.
Metal	K	Am	NH_4
Oxide	KO	$Am\,O$	NH_4, O
Chloride	KCl	$Am\,Cl$	NH_4, Cl
Sulphate	KO, SO_3	$Am\,O, SO_3$	$NH_4, O + SO_3$

The only difference between the two series is, that we know Am. to be a compound, while K is, as yet, undecomposed. But, as formerly remarked, all our present elements may hereafter prove to be compounds; and even were this not so, we can easily conceive a compound metal playing the same part as a simple one.

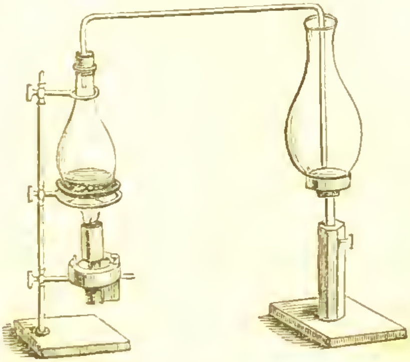
We have to bear in mind that ammonium, if it exists, is resolved into ammonia NH_3 and hydrogen, whenever we attempt to isolate it: that ammonia, in combining with a hydrated oxygen acid, such as HO, SO_3, takes the hydrogen of the water, forming ammonium NH_4, which, with the oxygen of the water, produces oxide of ammonium, and that the oxide then unites with the acid: and, finally, that ammonia, in contact with a hydrogen acid, such as HCl, takes the hydrogen of the acid to form ammonium, which then unites with the acid radical chlorine. Indeed, this very simple view may be extended to the hydrated oxygen acids, if we view them as hydrogen acids. Hydrated sulphuric acid, HO, SO_3, may be viewed as a hydrogen acid, H, SO_4: and if ammonia act on this, we have either $NH_3 + HO, SO_3 = NH_4, O, SO_3$: or $NH_3 + H, SO_4 = NH_4, SO_4$; the latter being perfectly analogous to the formation of chloride of ammonium (sal ammoniac), $NH_3, + HCl = NH_4, Cl$.

The above is a sketch of the ammonium theory of Berzelius, which is beautifully consistent, if we once admit the existence of ammonium: rendered, as it is, so probable by the phenomena of the amalgam, and by the isomorphism of the compounds of potash and those of ammonia + 1 eq. water. This theory is pretty generally adopted by chemists.

4. Chlorine. $Cl = 35{\cdot}47$.

This element occurs in prodigious quantity in the well known substance, sea or rock salt, in which it is combined with sodium. It is also occasionally found in combination with lead, silver, and mercury. Chloride of potassium is a frequent ingredient of ashes, especially of the ashes of sea plants.

It is best prepared by the action of peroxide of manganese on hydrochloric acid. 1 part of finely-powdered peroxide is covered in a roomy flask with 6 parts of moderately strong hydrochloric acid (4 parts of concentrated acid and 2 of water): to the flask is fitted tightly a tube bent twice at right angles, the longer limb of which is conducted to the bottom of a dry, wide-mouthed bottle, furnished with a tight glass stopper. The chlorine, on the application of a gentle warmth, escapes in the form of gas, and being much heavier than air, is very easily collected in dry vessels by displacement. As soon as the bottle is filled, which is easily seen from the yellow colour of the gas, it is withdrawn and replaced by another. If the gas is to be kept, the stopper must be tightly fitted into the bottle, and the juncture well greased.



The following equation shows the change :—$Mn\,O_2 + 2\,H\,Cl = Mn\,Cl + 2\,H\,O + Cl$. Here one half of the chlorine is given off as gas, while the other remains behind as chloride of manganese.

Chlorine at the usual temperature, is a gas which is liquefied by a pressure of about four atmospheres. It is transparent and of a strong yellowish-green colour (hence its name). Its Sp. G. is 2·500. Its smell is very disagreeable, pungent and suffocating; when much diluted it recals the smell of the air on the sea shore. If respired pure, it causes instant death; and even when diluted with air, excites cough, pain, and a sense of stricture on the chest, often lasting for many hours, and only relieved by a very copious expectoration of thick mucus, but occasionally followed by spitting of blood. The irritation thus caused may often give rise to permanent and serious disease of the lungs, and, therefore, care should be taken not to breathe the gas in working with it. It is not a little remarkable, however, that, if very much diluted, although still apt to excite cough, it is found to alleviate the symptoms of phthisis when inhaled, probably by promoting expectoration. The patients themselves soon learn to bear it stronger, and to long for the hour of inhaling it. It is also stated that the workers in manufactories of bleaching powder, and in bleaching and dye works, where the air is always to some extent charged with chlorine, are less liable to phthisis than others: so that, up to a certain point, the system seems capable of becoming habituated to it with benefit.

Chlorine supports the combustion of many substances, such as a candle; many take fire spontaneously in it, as phosphorus, antimony, oil of turpentine, &c. It may be made to burn itself in an atmosphere of hydrogen gas or coal gas.

Chlorine gas dissolves in water: hence it cannot be preserved over that liquid. The solution is termed chlorine water. It has the smell of the gas, and bleaches vegetable colours most powerfully, which perfectly dry chlorine does not. It also destroys fœtid or noxious effluvia, and is very useful in checking the spread of contagious disease.

The affinities of chlorine for the metals are very powerful, frequently stronger than those of oxygen. It therefore decomposes many oxides, as well as bromides, iodides, sulphurets, &c., at ordinary temperatures and almost all the rest at a red-heat. It acts so strongly on mercury that it cannot be collected over that metal. But its strongest affinity is to hydrogen, with which it forms hydrochloric acid. It is to this powerful affinity that the bleaching properties of chlorine are to be ascribed; it seizes on part of the hydrogen of the colouring matter, and thus decomposes it entirely. The same remark applies to the destruction of effluvia and miasmata.

The presence of free chlorine is detected by its smell and its power of bleaching solution of indigo. Nitrate of silver also causes with it a curdy white precipitate of chloride of silver, insoluble in acids. (See Hydrochloric Acid.)

The compounds of chlorine, which are not acids, are called chlorides.

SOLUTION OF CHLORINE.

This solution is prepared by simply passing a slow current of chlorine gas through water (previously boiled and allowed to cool), placed in inverted retorts nearly full. As soon as water begins to escape at the neck of one retort, the tube is transferred to another, and so on alternately till the water refuses to absorb any more. The solution, which has the colour, smell, and bleaching properties of the gas, must be kept in small bottles, quite filled, and closely fitted with glass stoppers. A drachm or more of this, added to about four or six ounces of water at 100°, forms a mixture through which air may be drawn into the lungs when we wish diluted chlorine to be inhaled. The solution is decomposed by light, and ought, therefore, to be kept in the dark.

Chlorine combines both with oxygen and hydrogen, but as the compound of chlorine with hydrogen is the most important, we shall here deviate slightly from the natural order and treat of it first.

CHLORINE AND HYDROGEN.

Hydrochloric Acid. $H\,Cl = 36{\cdot}47$.

SYN. *Muriatic Acid*—Is formed when equal volumes of chlorine and hydrogen are mixed and exposed to light, flame, or the electric spark, all of which cause the gases to combine with explosion. Is best prepared by the action of sulphuric acid on sea salt, when the gas is disengaged even without the aid of heat. As water instantly absorbs it, it must be collected over mercury, or by displacement, as it is somewhat heavier than air.

The following equation shows the formation of the acid :— $Na\,Cl + (H\,O, S\,O_3) = H\,Cl + (Na\,O, S\,O_3)$: or, $Na\,Cl + H, S\,O_4 = H\,Cl + Na, S\,O_4$.

Hydrochloric acid is a gas, transparent and colourless, fuming strongly with moist air, of a pungent, acid, suffocating smell, and a strong sour taste. Its Sp. G. is the mean between those of chlorine and hydrogen, or 1·284, it being formed of equal volumes of these gases without condensation. It is absorbed in large proportion by water, forming the common or liquid hydrochloric acid, which is merely a solution of the gas in water. This solution reddens, but does not bleach, vegetable blue colours ; and neutralises the alkalies, yielding neutral salts, which are found to be chlorides.

When it acts on soda, $Na\,O$, for example, we obtain neutral crystals by evaporation, but these are found to be sea-salt, $Na\,Cl$, and contain neither oxygen nor hydrogen, so that these latter elements must have united to form water ; thus : $Na\,O + H\,Cl = Na\,Cl + H\,O$. The result is, in regard to neutrality, the same as if the acid and alkali had directly combined together and neutralised each other : for the chloride of sodium ($Na\,Cl$) and water are both neutral. The general formula for the action of this and similar hydrogen acids on metallic oxides is as follows: $H\,R + M\,O = M\,R + H\,O$. Here, R stands for chlorine or any other acid radical, and M for any metal. If the oxide be a sesquioxide, the formula will be $3\,H\,R + M_2\,O_3 = M_2\,R_3 + 3\,H\,O$. Here, 3 eq. hydrogen acid and 1 eq. sesquioxide yield 1 eq. sesquichloride (bromide, iodide, &c.) and 3 eq. water ; but the principle is the same.

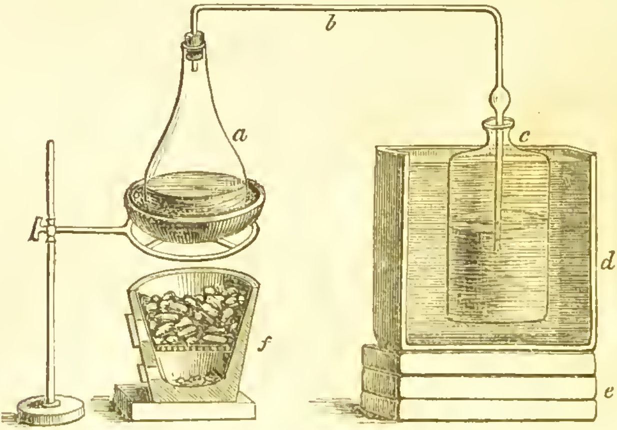
In some cases, however, hydrochloric acid appears to combine with oxides; as with alumina or oxide of chromium.

It will be easily seen, from what has just been said, that the action of hydrochloric acid on oxides affords a ready and convenient means of obtaining the corresponding chlorides. This method is very often employed.

HYDROCHLORIC ACID AND WATER.

Liquid, or Aqueous Hydrochloric Acid.

Syn. *Liquid Muriatic Acid: Spirit of Salt.*—This most indispensable re-agent is best prepared by the following easy process, which moreover yields it perfectly pure: 6 parts, by weight, of pure salt are introduced into a flask or matrass, and covered with ten parts, by weight, of oil of vitriol, and 4 parts of water, the latter having been previously mixed, and the mixture allowed to cool: or we may take 8·5 parts, by measure, of sulphuric acid, Sp. G. 1·65. No action takes place in the cold, so that we may adapt securely a bent tube to convey the gas to the flask. This tube is twice bent at right angles, and has a bulb blown on the longer descending limb. In a bottle, surrounded with ice-cold water, is placed a quantity of distilled water equal in weight to the salt, and the bent tube is made to dip about $\frac{1}{8}$ inch into this water. A gentle heat is now applied to the flask, which rests in a sand-pot, and continued as long as any hydrochloric acid comes over. In about two hours the process is finished, and we find the distilled water increased in volume nearly two-thirds, and converted into hydrochloric acid, quite pure and colourless, of Sp. G. 1·14



to 1·15. If we wish it as strong as possible, or of Sp. G. 1·21, we have only to employ, in a second operation, a part of the acid above described in the place of the distilled water, during the first half of the operation, when it will speedily become saturated. No safety-tube is required: it is only necessary to lower the bottle a little, occasionally, so that the tube shall never dip far into the liquid: and even should absorption take place too rapidly, and the water rise in the tube, the bulb will receive it, the end of the tube will be exposed, and air entering will prevent the regurgitation of the water into the flask. This simple tube, therefore, forms a self-acting valve, and renders a safety-tube unnecessary. The absorbing liquid must be kept as cold as possible, by frequently changing the surrounding water, which becomes warm owing to the heat developed in the absorption. If ice can be had, a little added to the cooling-vessel, from time to time, keeps the temperature sufficiently low.

In the above operation, the proportions of acid and salt are according to the formula

$$\mathrm{Na\,Cl}+2\,(\mathrm{HO},\ \mathrm{SO}_3)=(\mathrm{Na\,O},\ \mathrm{HO},\ 2\,\mathrm{SO}_3)+\mathrm{H\,Cl}.$$

Here, 2 eq. of acid are employed for one of salt; for two reasons. First, a much lower heat is required; and 2ndly, the resulting salt, bisulphate of soda, is quite easily got out, without risking the flask, which is not the case when 1 eq. of acid is used, and neutral sulphate is left. The acid is diluted to Sp. G. 1·65, or even 1·60 for the same reasons. The addition of the water facilitates the operation, and renders the resulting mass more soluble and manageable. It is to be observed that, notwithstanding this addition of water, $\frac{2}{3}$ of the hydrochloric acid gas comes off quite dry, and it is only towards the end of the operation that, the heat being increased, water and acid come off together. This is easily known by the tube becoming hot from the condensation of the steam. From first to last, not a trace of sulphuric acid passes over, even into the tube; and thus by using tolerably pure materials, we obtain colourless and pure hydrochloric acid, as easily and cheaply as if we were making the very impure acid of commerce. By the above process, the purest and strongest hydrochloric acid might be sold for not more than 3*d.* per lb., probably for less.

Pure aqueous hydrochloric acid has, when concentrated, a Sp. G. of 1·21, and fumes strongly when exposed to the air, the gas constantly escaping and uniting with the vapour which it meets. The acid even fumes when no denser than 1·13, and acid of from 1·14 to 1·16 is most convenient for common use, as there is not so much gas lost from it as from the strongest. It ought to be quite colourless ; if yellow, it contains perchloride of iron or free chlorine, probably both. The liquid is very acid and corrosive. When a rod dipped in āqua ammoniæ is brought near, very thick white fumes of sal ammoniac are formed. If heated, gas is expelled, the boiling point, which is at first very low, gradually rising, till the Sp. G. falls to 1·100, when the boiling point is rather higher than that of water; and at this strength the acid distils over unchanged. A weaker acid, if boiled, loses water, and becomes stronger, while a stronger, as we have seen, loses gas and becomes weaker. We can, therefore, purify the common acid by diluting it to Sp. G. 1·100, and distilling it, rejecting the first and last portions. The intermediate portion is pure, but cannot in this way be obtained concentrated.

The presence of hydrochloric acid is detected by nitrate of silver, which forms, even in very diluted solutions, a white curdy precipitate of chloride of silver, insoluble in acids. It is to be borne in mind, however, that the presence of free chlorine and soluble chlorides give rise to the same compound: we must, therefore, ascertain their absence, and the presence of an acid, before we can rely on this test.

The muriatic acid of commerce is very impure. It contains fixed impurities, detected by evaporation to dryness : sulphuric acid, detected by adding to the liquid, first distilled water, and then a salt of barium; chloride of iron, detected by ferrocyanide of potassium ; free chlorine, recognised by its power of dissolving gold ; and sulphurous acid, easily known by its smell. It often also contains tin and arsenic, which may be discovered by the proper tests of those metals. As no re-agent is so much employed by the chemist, and none so necessary to have perfectly pure, the chemist ought never, in careful experiments, to use the common acid ; and it is on this account that I have so minutely described the method which I have given for obtaining it pure, and which is now generally adopted in the Continental laboratories.

Hydrochloric acid is much used in chemical investigations, chiefly for dissolving inorganic bases, with most of which it forms soluble chlorides : the exceptions are oxide of silver and protoxide of mercury, the chlorides corresponding to which are insoluble ; and protoxide of lead, which yields a sparingly soluble chloride. In all inorganic researches, and, above all, in the analysis of minerals, soils, &c., it is absolutely indispensable.

Hydrochloric acid may be viewed as the type of all acids, including the so-called hydrated oxygen acids. We shall have occasion to return to this subject when treating of the acids of sulphur, and also in the general remarks on salts.

NITRO-MURIATIC, OR NITRO-HYDROCHLORIC ACID.

SYN. *Aqua Regia.*—This, which was formerly viewed as a distinct acid, and celebrated for its power of dissolving gold, is in reality a mixture. It is made by adding nitric acid to twice or thrice its bulk of strong hydrochloric acid. Both acids are decomposed, according to the equation :—

$$H\,Cl + NO_5 = HO + Cl + NO_4.$$

Here the products are water, chlorine, and nitrous acid. It is also possible that the change may be as follows :—

$$2\,H\,Cl + NO_5 = 2\,HO + Cl_2 + NO_3,$$

where the products are water, chlorine, and hyponitrous acid. While neither nitric nor hydrochloric acid, if pure, can dissolve gold or platinum separately, this mixture does so readily. It is certain, that free chlorine can dissolve those metals, and that their solution in aqua regia yields chlorides on evaporation; but there is reason also to believe, that the nitrous, or hyponitrous acids, contribute powerfully to the solvent power of the aqua regia, possibly by yielding oxygen to the metals, as these acids are more easily decomposed than nitric acid.

CHLORINE AND OXYGEN.

The affinity of chlorine for oxygen is very feeble, and these elements cannot be made to combine directly. By indirect means, however, they may be made to unite, and four compounds are known, all of which are acids.

a. Hypochlorous Acid. $Cl\,O = 43{\cdot}483$.

SYN. *Acide hypochloreux. Unterchlorige Saüre.*—When chlorine gas is passed through a cold diluted solution of an alkali, compounds are formed, which are known as bleaching compounds, and have been considered to consist of chlorine and metallic oxides, such as the so-called chlorides of lime and soda. They are, however, in reality, mixtures of chloride of the metal with hypochlorite of the oxide. Thus 2 eq. soda and 2 eq. chlorine, instead of combining together, act on each other as follows :—

$$2\,Na\,O + Cl_2 = Na\,Cl + Na\,O, Cl\,O.$$

The true bleaching compound of soda contains, therefore, 1 eq. of chloride of sodium+1 eq. hypochlorite of soda.

To obtain hypochlorous acid in the free state, red oxide of mercury and water are agitated with chlorine; when there are formed a compound of perchloride and peroxide of mercury, which is insoluble, and hypochlorous acid which dissolves in the water.

$$2\ Hg\ O_2 + Cl_4 = (Hg\ O_2 + Hg\ Cl_2) + 2\ Cl\ O.$$

By rectification, a stronger solution may be obtained; and if this be placed in a retort with an excess of dry nitrate of lime, this salt seizes on the water, and the hypochlorous acid gas separates, and may be collected over a saturated solution of nitrate of lime.

It is a gas of a strong yellow colour, and a peculiar penetrating smell. It is very easily decomposed into two vol. chlorine, and one vol. oxygen, exploding by the mere contact of many combustible substances, or by a gentle heat. Experiments with it require the greatest caution.

Water absorbs about 100 times its volume of this gas, and acquires a pale yellow colour, and the astringent, not acid, taste and peculiar smell of the gas. It bleaches powerfully, and is easily decomposed by all substances which have a strong affinity for chlorine or for oxygen.

With the stronger bases it unites, forming salts which are called hypochlorites, the general formula of which is $MO, Cl\ O$. With acids these salts yield hypochlorous acid, not chlorine, and they are thus distinguished from the true bleaching salts; which, when acted on by acids, yield pure chlorine. The bleaching salts have the general formula $M\ Cl + MO, Cl\ O$; that is, as already stated, they are mixtures or compounds of chlorides and hypochlorites. The action of sulphuric acid on them is as follows:

$$(M\ Cl + MO, Cl\ O) + 2\ SO_3 = 2\ (MO, SO_3) + Cl_2.$$

Here all the chlorine, both that of the chloride, and that of the hypochlorite, is given off in the free state. Hence, as chlorine is the real bleaching agent, the great bleaching power of the chlorides of lime and soda, as they are called. The action of dilute sulphuric acid on bleaching powder (chloride of lime, or $Ca\ Cl + Ca\ O, Cl\ O$,) furnishes a very easy and economical method of disengaging rapidly a large quantity of chlorine gas, as in fumigating a large room or house: no heat is required; we have only from time to time to add a table-spoonful of bleaching-powder to a basin of diluted acid.

When boiled, the hypochlorites as well as the bleaching compounds, which consist of hypochlorite+chloride, are resolved into chlorides and chlorates. Thus 3 eq. hypochlorite of potash, 3 (KO, Cl O,) yield 1 eq. chlorate of potash, $KO, Cl\,O_5$, and 2 eq. chloride of potassium, 2 K Cl. Of course, if, as in the bleaching compound of potash, the 3 eq. of hypochlorite were mixed with 3 eq. of chloride, the result would be 1 eq. of chlorate; and 5 eq. of chloride.

b. Chlorous Acid. $Cl\,O_4=67{\cdot}522$.

SYN. *Peroxide of Chlorine. Chlorige Saüre. Acide Hypochlorique.*—This acid is obtained by mixing oil of vitriol very gradually and cautiously with chlorate of potash, and applying to the yellow pasty mass thus formed, in a retort placed in a bath of proof spirit, a very gentle heat. Chlorous acid is given off as a deep yellow gas, which is even more easily decomposed, and more explosive than the preceding acid. Hence, very great caution, and the use of a glass mask, are necessary in experimenting with it. It may be collected over mercury. Its smell is peculiar, almost aromatic. It is absorbed by water, which acquires its odour, and its bleaching properties.

The following equation explains its formation :—

$$3\ (KO,\ Cl\,O_5)+(2\ SO_3)=KO,\ Cl\,O_7+2\ (KO,\ SO_3)+2\ Cl\,O_4.$$

That is, 3 eq. chlorate of potash, and 2 eq. sulphuric acid, yield 1 eq. perchlorate of potash, 2 eq. sulphate of potash, and 2 eq. chlorous acid.

The compounds of chlorous acid with bases are not much known. In contact with alkalies, chlorous acid appears to be resolved into chloric and hypochlorous acids. Thus, $4\ Cl\,O_4=3\ Cl\,O_5+Cl\,O$.

c. Chloric Acid. $Cl\,O_5=75{\cdot}535$.

SYN. *Hyperoxymuriatic Acid.*—This acid is formed, as we have seen, in combination with a base, under different circumstances; as, when the solution of a hypochlorite is boiled; when chlorine is passed through a hot and strong solution of an alkali; and when chlorous acid is brought in contact with bases. It is evident that in the second case a hypochlorite is formed, but is by the heat as rapidly destroyed, yielding a chlorite (see chlorate of potash); and if we suppose 6 eq. of potash to be acted on by 6 eq. chlorine, we may suppose the first stage to be represented as follows :—

$$6\ KO+Cl_6=3\ K\,Cl+3\ (KO,\ Cl\,O).$$

And in the second stage, the 3 K Cl remaining unchanged, we have

$$3\ (KO,\ Cl\,O)=2\ K\,Cl+(KO,\ Cl\,O_5).$$

Or, omitting the first stage, as temporary only in the heat, we have

$$6\ KO + Cl_6 = 5\ K\ Cl + (KO,\ Cl\ O_5).$$

To obtain chloric acid, chlorate of baryta is dissolved in water, and sulphuric acid is added, so as exactly to precipitate all the baryta as sulphate. The clear solution is concentrated by spontaneous evaporation.

When very strong, it forms a yellowish oily-looking liquid, very sour to the taste. A piece of paper dipped in it soon takes fire, from the ease with which the acid yields its oxygen. It is resolved by distillation into hyperchloric acid, oxygen, and chlorine.

$$2\ Cl\ O_5 = Cl\ O_7 + Cl + O_3.$$

The salts of this acid, which are called chlorates, are quite permanent, but readily explode with combustible matter at a red-heat; or, in some cases, by friction and percussion alone, or by contact of oil of vitriol. Thus phosphorus and charcoal explode most violently in contact with chlorate of potash—the latter by friction, the former by percussion; and a kind of instantaneous light, formerly much used, consisted of a mixture of chlorate of potash, sugar, and a little gum, to make it adhere, placed on the end of a match, and dipped into oil of vitriol, when it took fire. The lucifers now used are also made with the same salt, and take fire by friction. (See chlorate of potash.)

d. Perchloric Acid. $Cl\ O_7 = 91{\cdot}561$.

SYN. *Hyperchloric Acid.*—This acid may be obtained either by the distillation of chloric acid (see above), or by the distillation of hyperchlorate of potash with an equal weight of oil of vitriol, previously mixed with half as much water. It is purified from sulphuric acid by means of baryta, from chlorine by oxide of silver; and is then concentrated by slow evaporation.

It resembles the preceding acid, and when very concentrated, has a Sp. G. of 1·65. It reddens litmus without bleaching it, boils at 412°, and may be distilled without change. It is very permanent, and has strong affinities. Its best known salt is the perchlorate of potash, which is so sparingly soluble, that the acid may be used as a test for potash, in all liquids not too diluted. As the perchlorate of soda is very soluble, the use of this acid enables us to distinguish, and to separate soda from potash.

The perchlorate of potash is easily formed by melting chlorate of potash, and heating it till the mass becomes thick and pasty, which takes place when $\frac{1}{3}$ of the oxygen is expelled. The residue is a mixture of chloride of potassium and perchlorate of potash, and the latter is easily purified by dissolving the whole in hot water, and allowing it to crystallise on cooling. The action of heat on chlorate of potash is thus expressed:

$$2\ (KO, Cl\ O_5) = K\ Cl + (KO, Cl\ O_7) + O_4.$$

It must here be observed, that our knowledge of the compounds of chlorine and oxygen is far from being complete or satisfactory, and that Gay-Lussac and Millon, since the discovery by Balard of hypochlorous acid, have devoted attention to the subject. Millon, indeed, has published an elaborate memoir, in which he describes, under the name of chlorous acid, a compound ClO_3, while he gives to the chlorous acid above described the name of hypochloric acid. The compound discovered by Davy, by acting on chlorate of potash with hydrochloric acid, and by him called euchlorine, by others protoxide of chlorine, and supposed by some to be a mixture of chlorine and chlorous acid (ClO_4), by others to be identical with chlorous acid, is, according to Millon, composed of $Cl_3\ O_{13} = 2\ ClO_3 + ClO_7$. He calls it chlorochloric acid, and views it as composed of chlorous acid (ClO_3) and perchloric acid. In like manner, Millon has described another acid, obtained by the action of light on his chlorous acid in contact with cold water, and which he calls chloroperchloric acid. It is composed of $Cl_3O_{17} = ClO_3 + 2\ ClO_7$, and differs from the last in the proportion of chlorous and perchloric acids it contains.

Almost all of these compounds have properties so similar, that they are with difficulty distinguished from each other. Thus there are not less than 5 compounds, according to Millon, namely ClO, ClO_3, ClO_4, $Cl_3\ O_{13}$, and Cl_3O_{17}, which are volatile liquids, yielding deep yellow highly explosive vapours. He distinguishes ClO and ClO_3 from the others, as forming permanent salts with bases; the other three yield, with bases, a mixture of chlorate with chlorite (the acid in the latter being Millon's chlorous acid, ClO_3), and the proportion of these salts is different in each case.

We have not space to enter more minutely into this very difficult but interesting subject. The researches of Millon are hardly completed, and require confirmation. In the mean time, the following table contains the compounds admitted by him, with his view of their true constitution:

Hypochlorous acid . .	$Cl\ O$
Chlorous acid . .	$Cl\ O_3$
Hypochloric acid . .	$Cl\ O_4 = Cl_4\ O_{16} = 3\ Cl\ O_3 + Cl\ O_7$
Chloric acid . .	$Cl\ O_5 = Cl_2\ O_{10} = Cl\ O_3 + Cl\ O_7$
Chlorochloric acid . .	$Cl_3\ O_{13} = 2\ Cl\ O_3 + Cl\ O_7$
Chloroperchloric acid .	$Cl_3\ O_{17} = Cl\ O_3 + 2\ Cl\ O_7$
Perchloric acid . . .	$Cl\ O_7$

It will easily be seen that Millon admits, as independent compounds, only ClO, ClO_3, and ClO_7; and that he considers all the others as compounds of ClO_3 with ClO_7, in various proportions. This readily explains the formation of perchlorate of potash from chlorate: for, on this view, chlorate of potash is $KO, ClO_7 + KO, ClO_3$; and when heated, it is the latter (the chlorite) alone which is at first decomposed into chloride of potassium and oxygen. On this view, also, we see why all the three compounds, ClO_4, Cl_3O_{13}, and Cl_3O_{17}, have properties so similar, and why they all yield, with potash, mixtures of chlorate and chlorite. For the details of the preparation and properties of these compounds, I must refer to the memoir of Millon, which is in the *Annales de Chimie et de Physique*, 1843, also in Liebig's *Annalen*, xlvi., 281.

CHLORINE AND NITROGEN.

Perchloride of Nitrogen. $N\ Cl_4 = 156{\cdot}07$.

SYN. *Quadrichloride of Nitrogen.*—This compound is obtained by allowing chlorine gas to come in contact with a solution of sal ammoniac at 90° or 100°. The gas is slowly absorbed, and an oily liquid appears in large drops on the surface of the liquid. By agitating the vessel, these fall down, being heavier than the solution, and should be received in a thick cup of lead, kept very clean.

The chloride of nitrogen is a yellowish oily liquid, distinguished for its tendency to explode by the mere contact of combustible matter, such as fat, oil, essential oils, phosphorus, &c. &c. The explosion is so violent, that even one drop of the liquid infallibly shatters to pieces any basin or bottle in which it explodes; and as it explodes often without any obvious cause, possibly from the contact of some minute portion of greasy matter, it is most dangerous to experiment on. A strong mask should be worn, and all the vessels employed should be scrupulously clean if it is necessary to make such experiments; it is better, however, not to attempt them. Both Dulong, the discoverer, and Davy, suffered very severely from their researches on it. Each lost an eye, and the former lost several fingers also. For the sake of illustration, a drop or two may be exploded in the lead cup above mentioned, by simply touching them with a rod dipped in oil. The results of the explosion are chlorine and nitrogen gases. It is generally admitted that the formula of the compound is Cl_4N, and its formation may be thus explained—$NH_3, HCl + Cl_7 = 4HCl + NCl_4$.

5. Bromine. $Br = 78{\cdot}39$.

This element is found in minute proportion in sea water, in somewhat larger quantity in the water of the Dead Sea, in the bittern or mother liquor of sea water, out of which the sea salt has been crystallised, and in the mother liquid of many salt springs, from which, in like manner, the sea salt has been separated. The mother liquor of the salt springs at Kreuznach is particularly rich in bromine. In all these cases, the bromine occurs as bromide of potassium, sodium, or magnesium.

To obtain it, the liquor, concentrated as much as possible, is exposed to a current of chlorine gas, which is continued as long as the liquid becomes darker in colour from the bromine which is set free. The orange liquid thus obtained is to be agitated with ether, which rises to the surface, carrying with it all the bromine dissolved, which gives to the ether a hyacinth-red colour. The solution of bromine in ether is then acted on by a slight excess of potash, which produces a mixture of bromate of potash and bromide of potassium; $6KO + 6Br = 5KBr + (KO, BrO_5)$. The whole is dried up and ignited, when all the oxygen of the bromate is expelled, and only KBr is left. This bromide is mixed with rather more than half its weight of peroxide of manganese, and then distilled along with its own weight of oil of vitriol (previously mixed with half its weight of water); the red vapours of bromine are given off, and condensed in a tube or receiver very well cooled. By rectification with a little chloride of calcium, the bromide is obtained dry and pure. The following is the action of the sulphuric acid on the bromide of potassium and peroxide of manganese:—$KBr + MnO_2 + 2SO_3 = KO, SO_3 + MnO, SO_3 + Br$.

Bromine is, at ordinary temperatures, a deep brownish-red liquid, boiling at 113°; its Sp. G. is 2·99. Its vapour resembles that of nitrous acid, but has a very peculiar disagreeable pungent smell. It is poisonous, and acts so strongly on the living membrane of the nose, that the mere smelling to a bottle of bromine is often followed by a painful sensation in the nostril, attended with a copious flow of tears, lasting for hours, or even for days.

In all its relations, bromine is closely analogous to chlorine. It supports the combustion of phosphorus, and of many metals, like chlorine, and it bleaches organic colours. With hydrogen it forms hydrobromic acid, exactly analogous to hydrochloric acid; with oxygen it forms as yet only one acid, $Br\,O_5$, analogous to chloric acid. The analogy is equally striking when we compare the metallic bromides with the corresponding chlorides. Having so minutely described the relations of chlorine, this analogy will enable us to describe those of bromine very briefly. The affinities of bromine are less powerful than those of chlorine, so that the latter element disengages bromine from its compounds.

BROMINE AND HYDROGEN.

Hydrobromic Acid. $H\,Br = 79{\cdot}39$.

To obtain this acid, phosphorus, bromine, and a little water are placed in contact, and the gas which is disengaged is collected over mercury. The change is the following:—

$$P_2 + Br_3 + 3HO = P_2O_3 + 3H\,Br.$$

Here, along with hydrobromic acid, phosphorous acid is produced.

Hydrobromic acid is a gas, transparent and colourless, fuming strongly when mixed with the air. Its Sp. G. is 2·73. It is, in smell, taste, absorbability by water, and indeed all its properties, hardly distinguishable from hydrochloric acid; but chlorine decomposes it, setting free bromine. The strongest solution of the acid is a fuming liquid of Sp. G. 1·29.

With metallic oxides it forms water and bromides, exactly as was explained under hydrochloric acid.

$$MO + H\,Br = HO + M\,Br.$$

The bromides of lead, mercury, and silver, like the corresponding chlorides, are insoluble: the other bromides are soluble.

BROMINE AND OXYGEN.

Bromic Acid. $Br\,O_5 = 118{\cdot}445$.

It has been already mentioned that bromic acid is formed in combination with potash, when bromine is acted on by that alkali. The bromate of potash is quite analogous to the chlorate; and bromic acid may be obtained in the same way as chloric acid, by the action of fluosilicic acid on the bromate of potash, or of sulphuric acid on bromate of baryta. Its properties are quite analogous to those of chloric acid.

There is some reason to think that bromine forms bleaching compounds, which, like those of chlorine, contain peculiar acids, bromous or hypobromous acids ; and it is also probable that there exists a perbromic acid, analogous to perchloric acid. Our knowledge of these compounds, however, is very limited.

No compound of bromine and nitrogen is yet known. With chlorine bromine forms a reddish-yellow, volatile, pungent liquid, which is said to be $Br\,Cl_5$, a perchloride of bromine. When this substance is acted on by potash, it yields chloride of potassium and bromate of potash.

$$Br\,Cl_5 + 6\,K\,O = 5\,K\,Cl + (K\,O, Br\,O_5).$$

6. Iodine. I=126·57.

Iodine occurs in marine vegetables, and is found rather more abundantly in their ashes, as iodide of potassium, sodium, or magnesium. It is, of course, present in sea water, but in so small a proportion as not to be easily detected. Iodide of silver has been found in Mexico, and some of the Silesian ores of zinc contain iodine.

It is best obtained from kelp, the ashes of various species of fucus, or other algæ. The kelp is lixiviated with water and the solution evaporated as long as it deposits crystals. The mother liquor is precipitated by a mixture of 1 part of sulphate of copper and 2¼ parts of sulphate of iron, and the precipitate, which is sub-iodide of copper, $Cu_2\,I$, if heated with peroxide of manganese alone, or with the addition of sulphuric acid, yields the iodine as a purple vapour, which condenses in black crystalline scales on the cold part of the apparatus. It is purified by a second sublimation.

At ordinary temperatures iodine is solid, of a grayish-black colour, and metallic lustre, like plumbago. It is often seen in acute rhomboidal plates ; it is very brittle, and its Sp. G. is 4·948. It melts at 220°, and is converted, when dry, into purple vapour at 347°. Along with the vapour of water it volatilises much more easily. It has a peculiar marine smell and a rough acrid taste, and is poisonous.

Iodine is sparingly soluble in water, which takes up not more than $\frac{1}{7000}$ of its weight (1 lb. of water dissolves 1 grain of iodine). The solution has a pretty strong brownish-yellow colour, and the smell of iodine. Alcohol and ether dissolve iodine abundantly, forming deep-brown solutions. Free iodine, whether in the form of vapour or of solution, gives to starch a deep blue colour, which affords a very delicate test for iodine, as well as for starch.

Iodine, like chlorine and bromine, enters into combination with phosphorus, metals, &c., when placed in contact with them, and frequently with the phenomena of combustion.

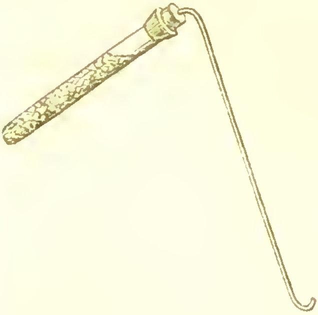
In liquids containing a minute trace of iodine in combination, it is best detected by adding fresh starch rubbed up with water, and then a very little chlorine, which may easily be done by simply inclining over the vessel the mouth of a phial containing some solution of chlorine, but not allowing the liquid to drop. There is always some chlorine gas in the upper part of the phial, which by its weight descends to the surface of the liquid to be tested, and the whole being agitated together, a blue tint, more or less deep, appears if iodine be present. Or oil of vitriol may be added to the liquid supposed to contain iodine, in a phial, and a slip of paper moistened with starch paste inserted between the cork and the neck of the phial, so as to be suspended over the liquid. After a time, if iodine be present, the starch is tinged blue. In both tests the iodine is set free, for combined iodine has no action on starch. In the chlorine test, the superior affinity of chlorine seizes on the metal with which the iodine is united—thus: $KI + Cl = KCl + I$.

In power of affinity iodine stands below bromine, as bromine does below chlorine. With metals it forms iodides extremely analogous to the chlorides and bromides. The iodides of lead, mercury, silver, and a few others are insoluble or sparingly soluble; most of the others are soluble. Some iodides possess beautiful colours, as those of lead and mercury. With hydrogen and oxygen iodine forms compounds, which, as far as they are known, correspond to those of chlorine and bromine with the same elements.

Iodine itself, and many metallic iodides, especially iodide of potassium, are much used in medicine as remedies in scrofula, and as discutients for glandular tumours in general. They are used both internally and externally in the shape of baths and ointments. Iodide of sulphur is also used medicinally. The long-known efficacy of burnt sponge was shown by Coindet to depend on its containing, as the ashes of sea-plants or zoophytes generally do, a small proportion of iodine. The presence of iodine has also been detected in certain mineral springs, both in South America and in Europe, which had acquired celebrity as capable of curing goître, a disease for which iodine seems to be a specific remedy, at least in all but the most advanced stages. On the whole, the discovery of iodine, which was made almost accidentally by Courtois, a soap-boiler, in Paris, in 1811, has proved a very valuable addition to the Materia Medica.

IODINE AND HYDROGEN.

Hydriodic Acid. $HI = 127{\cdot}57$.



This acid, which is exactly similar in properties to hydrochloric and hydrobromic acids, is best obtained, in the form of gas, by gently heating a mixture of one part of phosphorus and 16 of iodine, stratified with moistened sand or powdered glass, in a small tube. The gas may be collected over mercury, or absorbed by water, if the liquid acid is required. As iodine and phosphorus act very violently on each other, and indeed take fire in the open air, they ought to be brought in contact in the retort, and it is even preferable to fill it first with carbonic acid. Millon has lately proposed another method, namely, to dissolve in a very small quantity of water, in a retort or flask, some iodide of potassium, to add to this as much iodine as it will dissolve, and a moderate quantity of phosphorus in small pieces, and then to apply a gentle heat. In this way the action is more easily regulated.

Hydriodic acid gas is transparent, colourless, acid to the taste, and suffocating to the smell. It has a Sp. G. of 4·385, fumes strongly in the air, and is absorbed by water to as great an extent as hydrochloric acid gas, from which it is not to be easily distinguished, except by the action of chlorine or bromine, which, seizing the hydrogen, disengage the purple vapours of iodine.

The aqueous solution is prepared by passing a current of the gas through water, by passing a current of sulphuretted hydrogen through water in which iodine is suspended, or by adding diluted sulphuric acid to a solution of iodide of barium. The two latter methods are thus expressed:—

$$1.\quad I + HS = HI + S. \qquad 2.\quad Ba\,I + HO, SO_3 = HI + Ba\,O, SO_3.$$

When very concentrated, this solution acquires a Sp. G. of 1·700. It does not keep well, however, being decomposed by the oxygen of the air, with separation of iodine, $HI + O = HO + I$. With solution of bichloride of platinum, hydriodic acid strikes a deep brownish-red colour; with nitrate of bismuth a dark brown, nearly black. Hydriodic acid can dissolve a large quantity of free iodine, which gives it a deep brown colour; hence the gradual decomposition of the acid by the air is shown by its becoming continually darker, from dissolving the iodine separated.

With metallic oxides, this acid forms water and iodides. Thus, with solution of silver, it forms a yellowish-white precipitate of iodide of silver; with solution of lead, a fine yellow precipitate of iodide of lead; and with solution of peroxide or bichloride of mercury, a beautiful scarlet precipitate of biniodide of mercury. With chlorine and starch, it of course gives the blue iodide of starch.

IODINE AND OXYGEN.

a. Iodic Acid. $IO_5=166{\cdot}675$.

Analogous to chloric and bromic acids. To obtain it, iodine is boiled in a long-necked flask with the strongest nitric acid, when it is gradually oxidised, and the excess of nitric acid is expelled by a moderate heat. Or 9 parts of iodate of baryta are boiled with a mixture of 2 parts of oil of vitriol and 10 or 12 of water. The filtered liquid by evaporation yields iodic acid as a white crystalline solid.

It is very soluble in water and very acid to the taste. It is easily resolved into iodine and oxygen by a red-heat; and it also yields oxygen to many organic substances, and is used as a test for morphia or its salts, which it colours dark brown.

The salts of iodic acid, like the chlorates and bromates, deflagrate with combustible bodies at a red-heat, but not so powerfully as chlorate of potash. Iodic acid forms two series of salts, with 1 and 2 eq. of base respectively.

Iodic acid is decomposed, iodine being separated, by hydrochloric and hydrobromic acids, also by sulphuretted hydrogen and sulphurous acid. It may, therefore, be recognised by using any of these re-agents, followed by starch, to detect the free iodine.

b. Periodic Acid. $IO_7=182{\cdot}661$.

Analogous to perchloric acid. Formed when iodate of soda is heated with bleaching liquor (chloride of soda), or when chlorine is passed through a hot solution of 7 parts of dry carbonate of soda in 100 of water, in which 1 part of iodine is suspended, as long as a white crystalline salt is deposited. This is periodate of soda. It is dissolved in dilute nitric acid, and nitrate of lead added, which forms a precipitate of periodate of lead. This last salt is boiled with diluted sulphuric acid, avoiding excess, and the filtered solution, or evaporation, yields crystals of periodic acid, in transparent plates.

When heated, this acid is resolved into oxygen and iodic acid. It forms with bases two series of salts, with 1 and 2 eq. of base.

It is at present doubtful if there exist compounds of iodine with less oxygen than in iodic acid. Salts have been obtained, having a composition represented by MO, IO ; but the supposed hypoiodous acid, IO, has not been isolated, and these salts are very easily resolved into a mixture of iodates and iodides, of which they may possibly be, in reality, composed ; for $6\ (MO, IO) = 5\,MI + MO, IO_5$.

IODINE AND NITROGEN.

When iodine is placed in contact with aqua ammoniæ, there is formed a black powder, the composition of which is either NI_3 or NI_4. It explodes with very great violence, often spontaneously, on becoming dry by exposure to the air ; and at all times by very slight causes, a slight blow, or friction. It is, therefore, a very dangerous substance.

IODINE AND CHLORINE.

Iodine readily combines with chlorine, forming apparently two compounds, ICl and ICl_3, which, however, are not well known. Both of them are volatile liquids of a brown colour, and exceedingly pungent odour, strongly affecting the eyes. When acted on by alkalies, they yield iodate of the base and chloride of the metal, while iodine is set free. Water, also, decomposes them.

IODINE AND BROMINE.

Iodine appears, also, to form two compounds with bromine, of which one is solid, the other liquid. With alkalies they yield a mixture of iodate of the oxide and bromide of the metal, with free iodine.

7. Fluorine. $F = 18{\cdot}74$.

This element occurs in the mineral kingdom combined with calcium, as fluor spar ; also in small proportions as an element of mica and of topaz. Fluoride of calcium is also in minute quantity an ingredient of animal bones, especially of the enamel of the teeth, and of the urine of some animals. It is very remarkable, that fossil bones contain much more fluoride of calcium than recent bones; in some cases even 10 per cent. Even human bones of the historical period, as bones from the tombs of Egypt, or from Pompeii, appear to contain more fluoride of calcium than those of the present day.

Fluorine has not yet been isolated, owing, no doubt, to its very powerful affinities, which cause it, even if separated from one substance, instantly to unite with another, derived from the substance of the vessel used for the experiment. Its properties, in the separate state, are therefore unknown. Knox and Baudrimont have, of late, made repeated efforts to isolate fluorine, using vessels of fluor spar, &c., but as yet without satisfactory results; although it is conjectured, from some of these experiments, to be a yellow gas, not unlike chlorine. It is probable, however, that the presence of chlorine has been the cause of this apparent resemblance.

The affinities of fluorine for metals and for electro-positive elements in general, are very powerful indeed; probably surpassing those of oxygen. On the other hand, it has not been obtained in combination with any of the more negative elements, such as oxygen, chlorine, bromine, and iodine. These considerations render it probable that it is a highly negative body; and the character of its compounds with hydrogen and metals indicates a strong analogy between fluorine and chlorine, bromine and iodine.

FLUORINE AND HYDROGEN.

Hydrofluoric acid. $HF = 19{\cdot}74$.

Syn. *Fluoric acid.*—This acid is obtained by the action of oil of vitriol on fluoride of calcium (fluor spar). The powdered mineral is gently heated with the acid in a retort of lead, silver, or platinum, as glass and porcelain are destroyed by the process, and the acid condensed in a receiver of the same metal, surrounded by a freezing mixture. The action is thus expressed—

$$Ca\,F + H\,O, S\,O_3 = Ca\,O, S\,O_3 + H\,F.$$

The acid appears as a very volatile liquid, strongly acid and corrosive, fuming in the air. A drop on the skin burns it like red-hot iron, and causes a painful sore, not easily healed. Even the vapours, if they are allowed to come much in contact with the hand, are apt to cause painful sores under the nails. The acid, even when much diluted, or in the form of vapour, rapidly corrodes glass, and may be used for etching on glass plates.

With metallic oxides, hydrofluoric acid gives rise to water and metallic fluorides ; $HF+MO=HO+MF$. The affinity of fluorine for silicon is such, that hydrofluoric acid decomposes all silicious compounds ; and this explains its corrosive action on glass and porcelain. Berzelius has employed this acid as a means of analysing silicious minerals. As the fluoride of silicium is gaseous, any such mineral, if digested with hydrofluoric acid, soon loses all its silica, and is dissolved, so that the other ingredients may be determined.

No compound of fluorine with any of the preceding elements, except hydrogen, is yet known. Its compounds with silicon, boron, and the metals will come to be described in their natural places.

8. SULPHUR. $S=16{\cdot}12$.

Sulphur occurs, especially in volcanic districts, in a state of purity, often crystallised. It is also found in combination with oxygen, as sulphuric acid, in gypsum, heavy spar, and many other minerals, with hydrogen as sulphuretted hydrogen, in mineral waters, and above all with metals, most abundantly with lead, iron, copper, &c. &c. Finally, it is an essential ingredient of vegetable and animal fibrine, albumen, and caseine, and as such is indispensable to vegetation and to animal life. Some essential oils. such as those of mustard, of horse-radish, of assafœtida, &c., contain a large proportion of sulphur.

Native sulphur is purified by sublimation, when the sulphur assumes the form of a fine light powder, flowers of sulphur. It also occurs in cylindrical sticks, roll sulphur, which has been melted and run into moulds.

Sulphur is a solid of a pale yellow colour, of Sp. G. 1·99, and when pure has neither taste nor smell. It melts at 226° and boils at 600°, yielding a deep brownish-yellow vapour, or gas. At temperatures below 390° the melted sulphur is very fluid, but if heated to and beyond that point, it becomes so thick and viscid that it cannot be poured out of the vessel. If the heat be still increased, so as to approach the boiling point of sulphur, it again becomes fluid, although not so much so as at 230° or 240°. If now allowed gradually to cool, it first becomes thick, and on cooling still further, quite fluid again. When thrown into water in its most fluid state (at 240°), it instantly becomes a hard brittle yellow mass ; but if heated to between 500° and 600° for some time, and then thrown into water, it remains brown and transparent, and is so flexible that it may be kneaded in the fingers, and drawn into threads. In this state it may be used for taking copies of reliefs or intaglios, for in a few days it becomes solid, crystalline, hard, and yellow, retaining very sharp impressions.

Sulphur is a very bad conductor of heat and of electricity, hence it becomes strongly electric by friction. It crystallises in two distinct and irreconcilable forms, probably from a difference of temperature; from a solution in sulphuret of carbon, or chloride of sulphur, in acute rhombic octohedrons; and when melted and allowed to cool, in oblique rhombic prisms. It is thus dimorphous, and besides occurs in an altogether amorphous state when heated to 500° and thrown into cold water (*see above*).

Sulphur is insoluble in water, soluble in alcohol, ether, and oils, also in bisulphuret of carbon and in chloride of sulphur.

The affinities of sulphur are powerful; it forms numerous and important compounds, especially those with oxygen, hydrogen, and the metals. With many metals it combines when heated along with them, the combination being accompanied with the development of heat and light. In other words, metals undergo combustion with sulphur, just as with oxygen or chlorine. The compounds of sulphur with metals are called sulphurets.

Besides roll sulphur, and sublimed sulphur, there is another form, namely, precipitated sulphur or lac sulphuris. This is a light powder, nearly white, obtained by boiling sulphur with water and an alkali, and adding an acid to the solution, when sulphur separates as a precipitate. It is very finely divided, and appears to contain some water, although not perhaps chemically combined.

Sulphur is much used both externally and internally in medicine. It is a mild laxative, and acts as a specific when employed as ointment in prurigo and some other cutaneous affections.

When heated to above 560° in the open air, sulphur takes fire and burns with a blue flame, producing a very suffocating gas, which is sulphurous acid, the only compound of sulphur with oxygen capable of being formed by direct combination of its elements. There are, however, several other compounds of sulphur and oxygen, and one of them, the sulphuric acid, is perhaps the most important agent possessed by the chemist.

SULPHUR AND OXYGEN.

a. Sulphurous acid. $SO_2 = 32{\cdot}146$.

This is the gas produced when sulphur burns in the air or in oxygen gas. It is best obtained pure by heating oil of vitriol with mercury or copper. Either of these metals deprives a part of the sulphuric acid of oxygen, and the oxide thus formed combines with the rest of the acid. Thus—

$$Cu+2(HO, SO_3)=(Cu\ O, SO_3)+2\ HO+SO_2.$$

The gas may be collected over mercury, being absorbed by water.

Sulphurous acid is a transparent and colourless gas; it has a peculiar disagreeable taste and a most suffocating smell, and is very injurious when respired, its effects, such as hard cough, constriction in the trachea, &c., continuing for a long time. It is also very injurious to vegetation. Its Sp. G. is 2·222. It bleaches organic matters, such as flowers, without destroying the colouring matter as chlorine does; for the addition of a stronger acid produces the same red as if the colour had not been bleached. Sulphurous acid gas is liquefied by intense cold, and yields a very volatile liquid.

Water absorbs about 50 times its volume of this gas, forming liquid sulphurous acid, as it is called, properly an aqueous solution of the acid. This solution has the suffocating smell, peculiar taste, and bleaching properties of the gas. If exposed to the air, it gradually absorbs oxygen, and passes into sulphuric acid. Nitric acid also converts sulphurous acid into sulphuric acid.

With bases, sulphurous acid forms salts which are called sulphites. They have all the unpleasant taste of the acid, and when acted on by stronger acids, give off the suffocating smell of burning sulphur. These salts, as well as the acid, are occasionally used by the chemist as deoxidising agents, the sulphurous acid having a very powerful attraction for a third eq. of oxygen to form sulphuric acid. The oxides of mercury, silver, gold, and platinum, in solutions of their salts, are reduced to the metallic state by sulphurous acid.

b. Sulphuric acid. $SO_3=40·159$.

Oil of vitriol, or hydrated sulphuric acid $= HO, SO_3$ or $H, SO_4 = 49·272$.

The first of these formulæ represents dry or anhydrous sulphuric acid, or at least a substance having the composition of oil of vitriol, *minus* 1 eq. of water. But it is very doubtful if this compound really possesses acid properties; and we consider as true sulphuric acid the well-known compound oil of vitriol, which may be viewed either as a compound of water (a hydrate), or a compound of hydrogen (a hydrogen acid, analogous to hydrochloric acid).

Anhydrous sulphuric acid is obtained by distilling dried basic persulphate of iron, $Fe_2\ O_3,\ SO_3$, when the peroxide of iron is left, and the sulphuric acid distils over, condensing in the receiver (if kept dry) as a white crystalline solid, which gives off thick fumes in moist air, is converted into vapour at about 160°, and has so strong an affinity for the elements of water, that when thrown into water it hisses as a red-hot iron would do, combining with the water and forming oil of vitriol.

This compond, SO_3, enters into few combinations, and does not form the ordinary sulphates, unless the elements of water be present. Its claim to the character of an acid is therefore doubtful, and depends on the view which makes oil of vitriol a hydrate, $HO,\ SO_3$.

OIL OF VITRIOL, OR TRUE SULPHURIC ACID.

This acid cannot be formed by the direct union of its elements, but is produced by causing sulphurous acid to unite with an additional eq. of oxygen, in contact with the elements of water. Sulphur is burned with the aid of nitrate of potash or soda, thus yielding a mixture of sulphurous acid and nitrous acid gases. These gases are conducted into leaden chambers along with atmospherical air and steam, the bottom of the chambers being also covered with water. All the changes which take place are not thoroughly understood; but this much is certain, that the sulphurous acid is oxidised at the expense of the nitrous acid, reducing it to the state of deutoxide of nitrogen:

$$2\ SO_2 + NO_4 = 2\ SO_3 + NO_2.$$

The water becomes gradually charged with oil of vitriol, and the deutoxide of nitrogen, being reconverted into nitrous acid by contact with the oxygen of the air, again yields half its oxygen to a fresh portion of sulphurous acid; and thus, for an indefinite period, acts as a carrier of oxygen from the air to the sulphurous acid. In this way, a comparatively small quantity of nitrate is required for a large quantity of sulphur.

When the liquid has become very acid, it is boiled down in platinum or glass vessels until it acquires the Sp. G. 1·845, when it begins to be converted into vapour itself, all the superfluous water being now driven off. The remaining liquid is now oil of vitriol.

Oil of vitriol, or hydrated sulphuric acid, is an oily liquid, nearly twice as heavy as water, very acid and corrosive, charring all organic matters, apparently by its very strong attraction for water, or its elements. It freezes at—31°, and boils at 617°.

The oil of vitriol prepared at Nordhausen and other places, by the old process of distilling partially dried green vitriol (whence its name), often fumes on exposure to the air, and is called Nordhausen oil of vitriol, or fuming sulphuric acid. It is, in fact, a compound of 1 eq. anhydrous acid, and 1 eq. of common or hydrated sulphuric acid$=HO, 2\,SO_3$, or $HO, SO_3 + SO_3$. When the fuming acid of Nordhausen is distilled at about 290°, anhydrous acid distils over, and hydrated acid remains behind. Most specimens of the fuming acid contain 5 to 8 per cent. of hydrated acid, in excess beyond the formula $HO, SO_3 + SO_3$.

If we view common sulphuric acid as a hydrate of the anhydrous acid, then we have several hydrates of which the fuming acid is one. There are, 1st, fuming acid, $HO, 2\,SO_3$; 2d, common acid, HO, SO_3; 3d, $HO, SO_3 + HO = SO_3 + 2\,HO$; 4th, $HO, SO_3 + 2\,HO = SO_3 + 3\,HO$.

The third hydrate has a Sp. G. of 1·78, and at 39° crystallises in large regular transparent crystals. Of the two eqs. of water it contains, one is easily replaced by an eq. of a neutral salt; thus $HO, SO_3 + HO$ gives rise to bisulphate of potash ($HO, SO_3 + KO, SO_3$), when the 2d eq. of water is replaced by neutral sulphate of potash. The first eq. of water can only be displaced by an eq. of a base; as when HO, SO_3 gives rise to neutral sulphate of potash, KO, SO_3.

The 4th hydrate may be regarded as the third + 1 eq. water of crystallisation. Its Sp. G. is 1·632. If heated to 212°, it loses water, until nothing remains but the third hydrate.

If we view oil of vitriol, HO, SO_3, as the original compound from which all the others are derived, then the fuming acid will be a compound of 1 eq. of it with 1 eq. of anhydrous acid, and the other two hydrates will contain 1 eq. oil of vitriol, with 1 and 2 eq. of water respectively.

The attraction of oil of vitriol for water is very strong. When these liquids are mixed, a great amount of heat is developed, depending partly on the energetic chemical action, partly on the condensation which takes place; for the volume of the diluted acid, after cooling, is found to be considerably less than that of the acid and water before mixture. Oil of vitriol attracts moisture strongly from the atmosphere, becoming rapidly weaker if exposed. This property is made use of in Leslie's ingenious method of freezing water in vacuo by its own evaporation; the evaporation being greatly hastened by the presence of a vessel containing oil of vitriol, to absorb the vapour as fast as it is formed. In chemical researches, where heat is to be avoided, liquids are frequently concentrated by being placed either in vacuo, or simply under a bell-jar, along with a basin of this acid. Many gases, such as chlorine, carbonic acid, &c. &c., are most conveniently deprived of moisture by causing them to pass through oil of vitriol, which arrests all the water they contain. It is this powerful attraction for water that is the principal cause of the charring or corrosion of organic matters by this acid. When wood, for example, is charred by sulphuric acid, the acid is found to have undergone no further change, except that it is more diluted, having combined with water, the elements of which are derived from the wood. Now, as wood may be represented as carbon + water, the removal of water is, of course, accompanied by a separation of carbon.

No chemical agent is applied to a greater number of purposes in the useful arts than sulphuric acid; and hence its manufacture is of very high importance. Since the introduction and improvement of the process now followed, the price of this invaluable product has been diminished to a trifling fraction of what it was; and its applications have in consequence become vastly more numerous and important. These will be described in their proper places; but it may here be mentioned, that two of the most extensive and valuable chemical manufactures, those of soda from sea-salt, and of bleaching-powder, are entirely dependent on the supply of sulphuric acid at a low price; and that not only these manufactures have benefited by every reduction in the cost of making the acid, but also all the important arts to which soda and bleaching-powder are essential; such as soap-making, glass-making, and the cotton and calico-printing trades.

The uses of this acid to the scientific chemist are innumerable; almost every page of chemical works bears evidence of this. In medicine, diluted sulphuric acid is used as a refrigerant, and care should be taken to avoid administering it along with incompatible substances, such as all bases, and many salts.

The commercial acid is never pure. The chief impurities are sulphate of lead, derived from the lead chambers; arsenic, and occasionally selenium, derived from the sulphur; and nitrous, or hyponitrous acid. It is purified by distillation, the first portions being rejected, as containing the nitrous acid. The operation in glass vessels requires caution, as from the high temperature, and the tendency of the acid to boil with succussions, the retorts are liable to be broken. The danger is best avoided by introducing into the retort some coils of platinum wire, and heating chiefly from above, so that the ebullition may go on at the surface chiefly.

The pure distilled acid is perfectly colourless, and, when cold, devoid of smell; it ought also to be entirely dissipated when heated on platinum, leaving no residue.

The presence of sulphuric acid, whether free or combined, is detected in solutions by the characteristic property of forming, with any soluble compound of barium, a precipitate of sulphate of baryta, which is not only insoluble in water, but also in the strongest acids.

With bases, sulphuric acid forms salts, which are called sulphates. In the neutral sulphates, the water of the oil of vitriol is replaced by its equivalent of a metallic oxide; or, if we regard oil of vitriol as a hydrogen acid, then in the neutral sulphates the hydrogen is replaced by its equivalent of a metal. Thus we have

Oil of vitriol $= HO, SO_3$, or H, SO_4, and a
Neutral sulphate $= MO, SO_3$, or M, SO_4.

The acid in the neutral sulphates, as may be seen by their formula, contains three times as much oxygen as the base by which it is neutralised. This holds true also in the sulphates of sesquioxides, the formula of which is $M_2 O_3, 3 SO_3$, or $M_2, 3 SO_4$. The acid sulphates, which are numerous, contain twice as much acid as the neutral; thus acid sulphate, or bisulphate of potash, is $KO, HO, 2 SO_3$; when the acid contains six times as much oxygen as the base.

The affinity of sulphuric acid for most bases is stronger than that of all other acids. In a red heat, phosphoric and boracic acids, being fixed in the fire, expel sulphuric acid from its salts. In solution, sulphate of lime is decomposed by oxalic and racemic acids, which seize the lime; and sulphate of potash, by tartaric, racemic, and perchloric acids, which combine with the potash. In other circumstances, however, the sulphuric acid appears stronger than the acids just mentioned; thus, it decomposes phosphates in the cold, and tartrates, or perchlorates. with the aid of a gentle heat.

Many sulphates of metallic oxides, when exposed to a red heat along with charcoal, or in a current of hydrogen gas, lose all the oxygen they contain, and are changed into sulphurets of the metals. When charcoal is used, the oxygen escapes as carbonic oxide, or carbonic acid gas; when hydrogen is employed, the oxygen is given off as water. Thus, $MO, SO_3 + C_4 = 4\,CO + MS$; or $MO, SO_3 + H_4 = 4\,HO + MS$.

c. Hyposulphurous Acid. $S_2\,O_2 = 48{\cdot}266$.

This acid is unknown in the separate state. Its salts are formed when sulphur is boiled with a solution of sulphite. Thus, if sulphite of soda is boiled with sulphur, we have $Na\,O, SO_2 + S = Na\,O, S_2\,O_2$. The salts of this acid are called hyposulphites, and they are all, except the hyposulphite of baryta, easily soluble in water. Hyposulphites are also formed when alkalies are fused at a low heat with sulphur, and when solutions of alkaline sulphurets are exposed to the air so as to be slowly oxidised.

When we attempt to separate hyposulphurous acid from any of its salts, it is instantly resolved into sulphurous acid and sulphur, $S_2\,O_2 = SO_2 + S$. When oxidised by nitric acid, the hyposulphites are converted into bisulphates, $KO, S_2\,O_2 + O_4 = KO, 2\,SO_3$.

This acid, and all its soluble salts, possess the remarkable property of dissolving all the compounds of silver, even the chloride, which is insoluble in the strongest acids; and the solution thus formed has a very intense sweet taste, with a metallic after-taste. This property has been made available in the Daguerreotype, for the purpose of dissolving the sensitive coating of iodide from the plate of silver, after exposure to light, and thus fixing the image already formed. For this purpose hyposulphite of soda is now prepared in considerable quantity.

d. Hyposulphuric Acid. $S_2\,O_5 = 72{\cdot}355$.

This acid is formed, along with sulphuric acid, when sulphurous acid is oxidised by means of peroxide of manganese; $3\,SO_2 + 2\,Mn\,O_2 = Mn\,O, S_2\,O_5 + Mn\,O, SO_3$. The solution thus obtained is decomposed by baryta, or by sulphuret of barium, by which the manganese is separated as oxide or as sulphuret, and the sulphuric acid as sulphate of baryta, and hyposulphate of baryta, a soluble salt, is obtained; $Mn\,O, S_2\,O_5 + Ba\,S = Ba\,O, S_2\,O_5 + Mn\,S$; and $Mn\,O, SO_3 + Ba\,S = Ba\,O, S\,O_3 + Mn\,S$. The filtered solution is then mixed with just as much diluted sulphuric acid as is sufficient to separate the baryta as the insoluble sulphate, and the liquid now contains hyposulphuric acid; $Ba\,O, S_2\,O_5 + H\,O, SO_3 = Ba\,O, SO_3 + H\,O, S_2\,O_5$.

When concentrated by evaporation in vacuo, hyposulphuric acid forms a syrup liquid of a very acid taste, and devoid of smell. When heated, it yields sulphurous acid gas, while sulphuric acid remains, $S_2 O_5 = SO_2 + SO_3$. Its salts, when ignited, give off sulphurous acid, while sulphates remain; $MO, S_2 O_5 = SO_2 + MO, SO_3$.

With bases, this acid forms salts, most of which crystallise with great facility. It is not applied to any useful purpose.

e. Sulphuretted Hyposulphuric Acid. $S_3 O_5 = 88{\cdot}475$.

Discovered by Langlois. When bisulphite of potash is digested along with sulphur and water, without boiling, a salt is gradually produced, which contains this new acid. The acid may be isolated by means of perchloric acid, which removes the potash. It forms an acid liquid, which is slowly decomposed, and when heated is resolved into sulphurous acid, sulphur, and sulphuric acid; for $S_3 O_5 = SO_2 + S + SO_3$. The theory of its formation is not yet fully understood, and the acid itself is as yet but little known. The salt which it forms with potash crystallises easily, and when heated yields sulphurous acid, sulphur, and sulphate of potash; $KO, S_3 O_5 = SO_2 + S + KO, SO_3$.

f. Bisulphuretted Hyposulphuric Acid. $S_4 O_5 = 104{\cdot}595$.

Discovered by Fordos and Gelis. When iodine is dissolved in the solution of a hyposulphite, as hyposulphite of soda or baryta, the following change takes place:

$$2 (Ba O, S_2 O_2) + I = Ba I + Na O, S_4 O_5.$$

Here 2 eq. of hyposulphite of baryta and 1 eq. of iodine yield 1 eq. of iodide of barium and 1 eq. of the baryta salt of the new acid. Alcohol dissolves the former, and leaves the latter pure. By the cautious addition of diluted sulphuric acid, the baryta is precipitated, and the new acid is obtained dissolved in water. It resembles the two preceding acids, and, like the last, it is resolved, when heated, into sulphurous acid, sulphur, and sulphuric acid, $S_4 O_5 = SO_2 + S_2 + SO_3$. Here the quantity of sulphur separated is exactly double of that yielded by the acid last described.

The salts of this acid crystallise, and when heated yield 1 eq. of sulphurous acid, 2 eqs. of sulphur, and 1 eq. of sulphuric acid; $MO, S_4 O_5 = SO_2 + S_2 + MO, SO_3$.

The following table exhibits the composition of the compounds of sulphur and oxygen above described, with their formulæ, and those of their neutral salts, according to the older and newer views of the constitution of acids.

	Older View.		New View.	
	Acids.	Salts.	Acids.	Salts.
Sulphurous Acid . .	HO,SO_2	MO,SO_2	H,SO_3	M,SO_3
Sulphuric Acid . .	HO,SO_3	MO,SO_3	H,SO_4	M,SO_4
Hyposulphurous Acid .	HO,S_2O_2	MO,S_2O_2	H,S_2O_3	M,S_2O_3
Hyposulphuric Acid. .	HO,S_2O_5	MO,S_2O_5	H,S_2O_6	M,S_2O_6
Acid of Langlois . .	HO,S_3O_5	MO,S_3O_5	H,S_3O_6	M,S_3O_6
Acid of Fordos and Gelis	HO,S_4O_5	MO,S_4O_5	H,S_4O_6	M,S_4O_6

Now, when we reflect that all the salts in the above table, although containing only 1 eq. of metal or of base, are neutral, while the acids, according to the older view, and considered as oxygen compounds, contain different proportions of oxygen, we can hardly hesitate to prefer the newer view, according to which all true acids are hydrogen compounds, and their capacity of saturation, or power of neutralising bases, depends, not on the oxygen they contain, but on the amount of hydrogen replaceable by metals, which, in all these acids, is 1 equivalent. This at once accounts for the fact that acids so different in composition should all form neutral salts with the same quantity of base. The difference lies in the compound radicals, which, according to this theory, are united with hydrogen in the acids, and the composition of which may vary *ad infinitum* without affecting the neutralising power, provided the replaceable hydrogen continue unaltered. In fact, an acid has been described by Régnault in which 1 eq. of chlorine is added to the radical of sulphurous acid; and another by Pelouze, in which 1 eq. of hyponitrous acid is added to the same radical, without affecting the power of neutralisation.

If we take the radical of sulphurous acid as the first member of the series, all the above acids may be thus represented:—

Sulphurous Acid . . $H + SO_3$
Sulphuric Acid. . . $H + (SO_3 + O)$
Hyposulphurous Acid . $H + (SO_3 + S)$
Hyposulphuric Acid . $H + (SO_3 + SO_3)$
Acid of Langlois . . $H + (SO_3 + SO_3 + S)$
Acid of Fordos and Gelis $H + (SO_3 + SO_3 + S_2)$
Chlorosulphuric Acid . $H + (SO_3 + Cl)$
Nitrosulphuric Acid . . $H + (SO_3 + NO_3)$

Here we see that the addition to the radical SO_3 of oxygen, of sulphur, of its own elements SO_3, of the same with sulphur, of chlorine, or of hyponitrous acid, does not affect the neutralising power, that being dependent on the amount of replaceable hydrogen, which is the same in all.

I have here entered into some detail on the subject of the true constitution of acids, because the acids of sulphur form an admirable illustration of the superior simplicity of the new view of acids and salts, according to which, an acid may be defined as,—A compound of hydrogen with a radical, simple or compound, in which the hydrogen may be replaced by its equivalent of metal: while a salt is,—A combination of a simple or compound radical with a metal: the different salts of one metal corresponding with the oxides of the same metal.

It is obvious that even when a chemical combination or change is represented in a formula according to the old view, as is the case in almost all existing works, we can easily transpose the formula so as to express the new view. Thus, sulphate of potash, on the old view, is KO, SO_3; on the new it is K, SO_4; or if we express the action of iron on sulphuric acid, on the former view, by $Fe + HO, SO_3 = H + FeO, SO_3$ it is more simple on the latter, $Fe + H, SO_4 = H + Fe, SO_4$.

While, therefore, in order to avoid confusion, I shall generally use, in equations, the older formula for acids and salts, I shall give the new formula for the principal acids, as I have done for sulphuric and nitric acids, so that the student may, if he please, convert the equations into the new form.

SULPHUR AND HYDROGEN.

a. Sulphuretted Hydrogen. $HS = 17{\cdot}12$.

SYN. *Hydrosulphuric Acid.*—This compound is formed when hydrogen and sulphur come in contact in the nascent state. It is best prepared by causing diluted hydrochloric or sulphuric acid to act on sulphuret of iron in the apparatus, p. 49, when sulphuretted hydrogen is disengaged as a gas, which may be collected over warm water, or solution of salt. The action is as follows: $FeS + HCl = FeCl + HS$.

Sulphuretted hydrogen is a gas, transparent and colourless, having a very offensive and peculiar smell, which is well known as that of putrid eggs. It is liquefied by a pressure of 17 atmospheres. When respired, even although much diluted with air, it is highly deleterious, and as it is often formed where animal matters or excrements putrefy, as in burying-vaults and cloacæ, it not unfrequently causes the death of workmen who suddenly come in contact with it. The smell of the gas ought, in all cases, to be viewed as a warning of danger. The presence of the gas may also be recognised by its power of blackening the salts of lead, owing to the formation of the black sulphuret of lead.

This gas is combustible, burning with a bluish flame, and producing sulphurous acid gas and water. Its Sp. G. is 1·177. Water absorbs 2 or 3 times its volume of the gas, and acquires its smell and a nauseous sweetish taste. By contact with the air, the solution is gradually decomposed: water is formed and sulphur deposited. Sulphuretted hydrogen water must, therefore, be kept in small phials, quite full and closely stopped.

Sulphuretted hydrogen has the properties of a weak acid; it reddens litmus feebly, and acts on bases, forming with them water and metallic sulphurets: $HS + MO = HO + MS$. As the sulphurets of some metals are soluble while those of others are insoluble; as moreover the oxides of some of the latter are not decomposed by sulphuretted hydrogen when dissolved in an acid, the action of this gas on solutions of metals in acids affords us a great deal of information, according as a precipitate of sulphuret is formed or not, the colour of the precipitate being also frequently characteristic, as will be described under the individual metals: this renders sulphuretted hydrogen a most useful re-agent in detecting and separating from each other metallic compounds.

Mineral waters exist, as at Harrogate, which contain sulphuretted hydrogen, easily recognised by its smell and by the property of blackening the salts of lead, silver, and several other metals. The gas in these waters arises from the slow and continued putrefaction of vegetable matters containing sulphur, such as albumen, fibrine, &c. These sulphureous waters are used in medicine, both internally and externally (as baths), with great advantage. In many cases the artificial sulphuretted hydrogen water, formed by passing the gas through water, previously boiled and allowed to cool, may be substituted for them.

b. Persulphuretted Hydrogen. HS_5? or HS_2?

This compound is formed when alkalies, such as potash or lime, are boiled with excess of sulphur, and the solution, which is of a deep yellow or orange colour, is poured into a large excess of moderately strong hydrochloric acid, made by mixing equal parts of concentrated acid and water. A heavy, somewhat viscid, transparent, yellowish liquid falls to the bottom, which is the compound in question. The precise nature of all the changes which take place in this process is not known;

but it is probable that a persulphuret of the metal is formed in the first stage, such as persulphuret of potassium KS_5; and that a hyposulphite is generated at the same time, possibly according to the formula $3KO + S_{12} = KO, S_2O_2 + 2KS_5$. In the second stage, we have probably $KS_5 + HCl = KCl + HS_5$. But as the composition of persulphuretted hydrogen is not precisely determined, and as the persulphuret appears to dissolve an excess of sulphur, we cannot be certain that this is the true explanation. Thénard considers persulphuretted hydrogen HS_2, and to be analogous to the peroxide of hydrogen HS_2. But his own analysis always gave far more sulphur than corresponds to his formula, and the analogy he pointed out is very obscure and doubtful.

Persulphuretted hydrogen soon undergoes spontaneous decomposition, even if kept in sealed tubes, resolving itself into sulphur and sulphuretted hydrogen. In a strong sealed tube, the sulphuretted hydrogen, by its own pressure, is liquefied, and floats above the sulphur, which is deposited in transparent crystals. Persulphuretted hydrogen seems to have feeble acid properties. In contact with alkalies, it reproduces water and the metallic persulphuret. $HS_5 + KO = HO + KS_5$.

SULPHUR AND NITROGEN.

Sulphuret of Nitrogen. $NS_3 = 62{\cdot}51$.

When chloride of sulphur, SCl, acts on dry ammonia, NH_3, a compound is formed, $SCl, 2NH_3$. By the action of water on this there is formed, among other products, a greenish yellow solid body, which is sulphuret of nitrogen NS_3. By contact with water, it is gradually converted into hyposulphurous acid and ammonia: for $2NS_3 + 6HO = 2NH_3 + 3S_2O_2$.—(Soubeiran).

When aqua ammoniæ acts on chloride of sulphur, a variety of products are formed, among which is one, a white crystallisable solid, soluble in alcohol, which appears to consist chiefly of sulphur and nitrogen. Its nature is not yet ascertained, but it is distinguished by the property of dissolving in an alcoholic solution of potash with a deep purple colour, which soon disappears, while ammonia is given off, and crystals of hyposulphite of potash are deposited.—(W. G.)

SULPHUR AND AMMONIUM.

a. Protosulphuret of Ammonium. $NH_4, S = Am S = 34{\cdot}27$.

Syn. *Hydrosulphuret of Ammonia.*—This compound is formed when 1 vol. of dry ammoniacal gas is mixed with ½ vol.

of sulphuretted hydrogen, $NH_3 + HS = NH_4, S$. It is best obtained by distilling a mixture of chloride of ammonium (sal ammoniac) and sulphuret of barium, or of calcium. $BaS + NH_4, Cl = Ba\,Cl + NH_4, S$. It forms colourless crystals, which are volatile, and dissolve readily in water. The solution becomes yellow by the gradual action of the atmospheric oxygen; it smells of sulphuretted hydrogen and ammonia; and in fact this solution may be more conveniently prepared by taking two equal portions of aqua ammoniæ, and saturating one of them completely with sulphuretted hydrogen. This produces, first, sulphuret of ammonium, and then a compound of that body with sulphuretted hydrogen, $NH_4, S + HS$. The other half of the aqua ammoniæ is then added, and we have $(NH_4, S + HS) + NH_3 = 2\,(NH_4, S)$.

Sulphuret of ammonium, or hydrosulphuret of ammonia, as it is called, is very much used as a test and re-agent in detecting and separating metals. It converts into sulphurets many oxides on which sulphuretted hydrogen does not act, and it also dissolves many metallic sulphurets.

The compound above mentioned, which is formed when ammonia is completely saturated with sulphuretted hydrogen, $NH_4, S + HS$, possesses very nearly the same properties, and may be used for the same purposes. It may be called the hydrosulphuret of sulphuret of ammonium.

Both the preceding compounds, when pure, are colourless; and their solution, mixed with acids, gives off sulphuretted hydrogen, without the deposition of sulphur. By keeping, however, they become yellow, and acids cause a precipitation of sulphur. This is owing to the formation of persulphuret of ammonium.

b. Persulphuret of Ammonium.

This compound is formed when either of the preceding is digested with sulphur. There seem to be several sulphurets of ammonium, as of potassium (which see), containing from 2 to 5 eqs. sulphur. When NH_4, S is exposed to the air, we may suppose the ammonium of 1 eq. to be oxidised (as is the case with potassium) and to be converted into free ammonia, $NH_4, O = NH_3, HO$, while the sulphur of that equivalent unites with the other, forming NH_4, S_2. When the compound $NH_4, S, + HS$ is exposed to the air, it is the hydrogen of the sulphuretted hydrogen which is oxidised, while its sulphur forms the bisulphuret of ammonium. When sulphur is digested with either of the preceding compounds, different persulphurets of ammonium are probably formed; and where the sulphur is in excess, it yields, in all probability, the compound NH_4, S_5, analogous to persulphuret of potassium, KS_5.

All the yellow sulphurets of ammonium have the same useful properties as the protosulphuret in relation to metallic compounds, and some of them dissolve certain metallic sulphurets still more readily. The persulphuret of ammonium or sulphuretted hydrosulphuret of ammonia, as it is sometimes called, is, therefore, very much used in analysis. It is distinguished from the protosulphuret by the action of acids, which cause a precipitate of sulphur, and by its yellow or orange colour. The solution of protosulphuret of ammonium, when kept, becomes gradually yellow, from the formation of persulphuret; so that, in fact, the latter is always present in the usual forms of this valuable re-agent.

Sulphuret of ammonium, under the name of hydrosulphuret of ammonia, is used in medicine. It ought to be given alone, in pure water, as it is decomposed by most acids or salts. The persulphuret has long been known as Boyle's fuming liquor, which was obtained by distilling 3 parts of slaked lime, 2 of sal-ammoniac, and 1 of sulphur, into a receiver containing 3 parts of water. Thus prepared, it was an orange-coloured liquid, of oily consistence, fuming in the air, and having a very offensive sulphurous smell. This preparation, however, contains variable proportions of free ammonia.

SULPHUR AND CHLORINE.

a. Dichloride of sulphur. $S_2 Cl = 67{\cdot}71$.

Formed when chlorine is passed through a vessel containing flowers of sulphur, until nearly the whole sulphur has disappeared. The liquid formed is then purified by distillation. It is a reddish brown, fuming, pungent liquid, boiling at 280°. The Sp. G. of the liquid is 1·687; that of the vapour is 4·70. It is decomposed by water, yielding hydrochloric acid, hyposulphurous acid, and sulphur.

b. Protochloride of sulphur. $S Cl = 51{\cdot}59$.

When an excess of chlorine is passed through the preceding compound, and the liquid is repeatedly distilled at about 140°, the protochloride is obtained pure. It is a deep reddish brown liquid, which boils at 147°. Its Sp. G. is 1·62; that of its vapour, 3·68. When acted on by water, it yields hydrochloric acid and hyposulphurous acids, the latter being soon spontaneously decomposed, $2 S Cl + 2 H O = 2 H Cl + S_2 O_2$.

SULPHUR AND BROMINE.

Bromine combines readily with sulphur, and produces compounds analogous to the preceding.

SULPHUR AND IODINE.

When 1 part of sulphur and 8 of iodine are mixed and gently heated, they immediately combine and liquefy. On cooling, the liquid, which is dark brown, consolidates into a black crystalline solid, which is the iodide of sulphur. It must be kept in well-closed bottles, as it is destroyed by the access of air, iodine being given off. Its composition is probably $S\,I$. It is used in medicine as a remedy in various cutaneous diseases.

No compound of sulphur and fluorine is yet known.

9. SELENIUM. $Se = 39{\cdot}6$.

This element occurs in very small quantity, chiefly in certain varieties of pyrites, the sulphur from which, when converted into sulphuric acid, leaves in the chambers a deposit, consisting of sulphur, selenium, and some metals; and from this the selenium is obtained. Some kinds of fuming sulphuric acid contain a little selenium, which separates on the addition of water as a red powder. Different processes are employed for extracting selenium from the deposit above mentioned; but the essential parts are, oxidising and dissolving the selenium by means of aqua regia, separating the dissolved metals by sulphuretted hydrogen, &c., and finally deoxidising the selenious acid by means of sulphite of ammonia and hydrochloric acid.

When precipitated, selenium appears as a red powder, which, when heated, melts, and on cooling forms a brittle mass, nearly black, but transmitting red light in thin plates. When more strongly heated it volatilises, yielding a yellow gas, which condenses into a crystalline dark red powder on a cold surface.

Selenium is extremely analogous to sulphur, except in colour; and this analogy is still more striking in its combinations. When heated in the air it takes fire, burns with a blue flame, and produces a gaseous compound, oxide of selenium, $Se\,O$, which has a most penetrating and characteristic odour of putrid horse-radish. By this character selenium is easily recognised in minerals containing it, before the blowpipe.

SELENIUM AND OXYGEN.

These elements combine in three proportions—

a. Oxide of Selenium. $Se\,O = 47{\cdot}613$.

This compound has been already mentioned. It is formed when selenium burns, and is gaseous; it is not acid, and has no analogy with any of the oxides of sulphur.

b. Selenious Acid. $Se\,O_2 = 55{\cdot}626$.

This acid is formed when selenium is dissolved in nitric acid, and the solution evaporated to dryness. It is a solid which, when heated, is converted into a yellow gas, condensing again into acicular crystals. It is very soluble in water, and has an acid taste. In composition it corresponds to sulphurous acid. This latter acid and its salts deprive selenious acid and its salts of oxygen, causing the selenium to be deposited in the uncombined state.

c. Selenic Acid. $HO, Se\,O_3 = H, Se\,O_4 = 72{\cdot}652$.

This acid is formed when selenium is oxidised by fusion with nitre. The fused mass is dissolved in water, and the selenic acid precipitated as seleniate of lead by adding a salt of lead. The seleniate of lead is decomposed by sulphuretted hydrogen, and the filtered solution of selenic acid cautiously evaporated till it has the Sp. G. 2·625. It is now hydrated selenic acid, $H\,O, Se\,O_3$, or rather $H, Se\,O_4$. It is very acid and corrosive, and resembles sulphuric acid very much. It may be recognised by the action of hydrochloric acid, which reduces it to selenious acid, chlorine being set free. Selenic acid is not decomposed by sulphurous acid (as selenious acid is), or by sulphuretted hydrogen. It produces intense heat when mixed with water.

With bases, for which it has great affinity, selenic acid forms salts, called seleniates, which are isomorphous with the corresponding sulphates, and entirely resemble them in external characters.

SELENIUM AND HYDROGEN.

Seleniuretted Hydrogen. $H\,Se = 40{\cdot}6$.

SYN. *Hydroselenic acid.*—This compound is obtained, like sulphuretted hydrogen, which it much resembles, by the action of acids on metallic seleniurets. $M\,Se + H\,Cl = M\,Cl + H\,Se$.

It is a colourless gas, which is combustible, and when burned gives off the characteristic odour of oxide of selenium. Seleniuretted hydrogen itself has a smell resembling that of sulphuretted hydrogen, and when respired is even more poisonous than that gas. A small bubble of it produces much and painful irritation of the mucous membrane of the nose and eyes; and if it reaches the bronchi, excites severe cough, in addition to its poisonous action if absorbed into the blood. The presence of a small quantity of it in sulphuretted hydrogen seems to exalt the poisonous energy of the latter. Like sulphuretted hydrogen, this gas is absorbed by water, and precipitates most metallic solutions, yielding seleniurets corresponding to the respective oxides. Most of these seleniurets are black or dark brown; but those of zinc, manganese, and cerium, are flesh red.

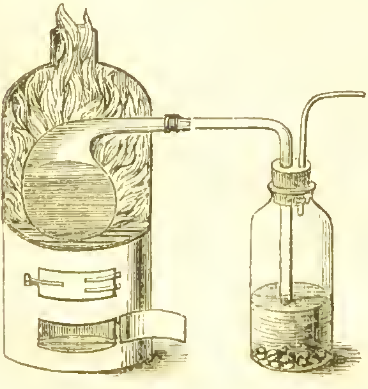
Nothing is known of the compounds of selenium with nitrogen. With ammonia it is probable that seleniuretted hydrogen forms seleniuret of ammonium, NH_4, Se, and hydroseleniuret of seleniuret of ammonium, NH_4, Se + H Se.—(Bineau.)

Chloride of selenium appears to be analogous to chloride of sulphur; and the same may be said of the bromide and iodide.

10. Phosphorus. P=15·7.

This element occurs abundantly in the bones of animals, in combination with oxygen and metals, as phosphate of lime, phosphate of magnesia, &c. It is also an ingredient in some unknown form of combination, of vegetable and animal fibrine and albumen, and is constantly present in the urine and excrements. In the mineral kingdom it occurs as phosphate of lime (apatite), phosphate of alumina (wavellite), phosphates of lead, copper, &c.

To obtain phosphorus pure, 10 parts of burnt bones are mixed with 30 or 40 parts of water, and 6 parts of oil of vitriol gradually added. After 24 hours, 50 or 60 parts of water are added to the mixture, and the whole well stirred and digested for a day or two. The strained liquid is evaporated to the consistence of thick syrup, and is then acid phosphate of lime. It is now mixed with ¼ of its weight of powdered charcoal, dried up, and gently ignited. The mass is then gradually heated to whiteness in a stoneware or iron retort, the neck of which ends in a wide bent tube, which dips a little under water. Half of the phosphoric acid in the acid phosphate of lime is deoxidised by the charcoal, and phosphorus is set free, which distils over, and condenses under the water. Owing to the presence of water in the mass, part of the phosphorus is disengaged in combination with hydrogen, forming a spontaneously com-



bustible gas. Care must therefore be taken to avoid explosions. The action of the charcoal on the phosphoric acid is thus represented—$P_2O_5 + C_5 = 5CO + P_2$. Carbonic oxide gas, CO, is therefore disengaged in large quantity.

The phosphorus is now to be melted under water, and squeezed through chamois leather, which separates impurities. It is lastly melted under water, in funnels with long cylindrical necks, stopped below. Into the necks of the funnels the phosphorus runs, and when cold may be pushed out in the form of solid cylinders.

Pure phosphorus is a colourless, or very pale, yellowish, transparent, or translucent solid, of the consistence of wax. Its Sp. G. is 1·77. At 113° it melts, and at 572° it boils, distilling completely in close vessels. It has, in the solid form, neither taste nor smell; but it gives off vapours in the air, which, undergoing a slow combustion, have an odour of garlic; and in solution it has an acrid disagreeable taste. Phosphorus is insoluble in water, soluble in alcohol, ether, oils, sulphuret of carbon, and chloride of phosphorus. From the latter liquids it is often deposited in octahedral and dodecahedral crystals. It is very poisonous, but is used in medicine in very small doses.

When kept in vessels exposed to light, phosphorus becomes yellow, or even brown, externally, owing to some unexplained change. It must always be kept under water, and never taken into the fingers, for it is so combustible as occasionally to take fire from contact with the warm hand, where, as it melts and continues to burn, it inflicts frightful injuries.

When heated in air, phosphorus takes fire, and burns with a bright light, producing much white smoke, which is anhydrous phosphoric acid, P_2O_5. When heated in oxygen, it burns with a light so dazzling that the eye cannot endure it. In contact with chlorine, bromine, or iodine, without the aid of heat, combustion takes place spontaneously, while the phosphorus combines with these metalloids.

PHOSPHORUS AND OXYGEN.

Phosphorus combines very readily with oxygen. Even at the ordinary temperature it undergoes a slow combustion in air, giving out vapours, which are luminous in the dark. It frequently happens that the heat developed by this slow combustion gradually reaches the point at which the phosphorus takes fire; hence the spontaneous combustion of phosphorus, if left exposed to the air, and the necessity of keeping it under water. Many powders, such as powder of platinum, charcoal.

lamp-black, &c., when sprinkled on dry phosphorus, cause it to take fire ; no doubt because these powders absorb and condense oxygen in their pores, and thus bring it into close contact with the phosphorus.

Many different kinds of instantaneous lights are made with phosphorus, owing to its ready combustibility by friction, especially when chlorate of potash is used.

We are acquainted with four compounds of phosphorus and oxygen.

a. Oxide of Phosphorus. $P_3O = 55{\cdot}113$.

This oxide is obtained by causing a current of oxygen to come in contact with phosphorus under boiling water. Combustion takes place, and some phosphoric acid is formed ; but a part of the phosphorus forms an insoluble cinnabar red powder, which is oxide of phosphorus, P_3O.

It burns, if heated nearly to redness, in the air ; if heated in close vessels, it is resolved into phosphorus and phosphoric acid, $5P_3O = P_2O_5 + P_{13}$. It is oxidised with combustion by nitric acid, and takes fire in chlorine gas.

b. Hypophosphorous Acid. $P_2O = 39{\cdot}413$.

In the separate, or hydrated state, $P_2O, 3\,HO$, or P_2O_4, H_3. This acid is formed when phosphurets of the alkaline metals act on water, or when phosphorus is boiled with alkalies and water, phosphoric acid and phosphuretted hydrogen gas being formed at the same time. The two acids combine with the base ; and if this be lime or baryta, the hypophosphite being soluble, is easily separated from the insoluble phosphate. From the hypophosphite of baryta, sulphuric acid removes the baryta, and the hypophosphorus acid is left, dissolved in water. By gentle evaporation it may be obtained as a deliquescent crystalline mass, which is the hydrated acid.

When heated in close vessels, this acid is resolved into phosphuretted hydrogen gas and phosphoric acid. Thus, $2\,(P_2O, 3\,HO) = P_2H_3 + P_2O_5, 3\,HO$. It is a powerful deoxidising agent, taking oxygen from many other substances, and passing into phosphoric acid. With bases, it forms salts called hypophosphites, which are all soluble in water, and which, when heated, are resolved into phosphates and phosphuretted hydrogen.

c. Phosphorous Acid.

In the anhydrous state, P_2O_3 ; in the separate, or hydrated, state (the crystals), $P_2O_3, 3\,HO$, or P_2O_6, H_3.

This acid is formed, along with phosphoric acid, during the slow combustion of phosphorus in air. It is best obtained pure by acting on the sesquichloride of phosphorus, P_2Cl_3, by water. $P_2Cl_3+6\,HO=3\,HCl+P_2O_3\,3\,HO$. The hydrochloric acid is easily expelled by a gentle heat, and the aqueous solution of phosphorous acid, if sufficiently evaporated, yields a mass composed of deliquescent crystals. This is the hydrated acid.

This acid, like the preceding, is a powerful deoxidising agent. When heated in close vessels, the anhydrous acid, obtained by the combustion of phosphorus in rarefied air, yields phosphorus, and anhydrous phosphoric acid, $5\,P_2O_3=3\,P_2O_5+P_4$. The hydrated acid, in the same circumstances, yields hydrated phosphoric acid and phosphuretted hydrogen gas, $4\,(P_2O_3, 3\,HO)=3\,(P_2O_5, 3\,HO)+P_2H_3$.

With bases phosphorous acid forms salts, which are called phosphites; and the general formula of the neutral phosphites is $P_2O_3, 3\,MO$, or P_2O_6, M_3.

d. Phosphoric Acid.

1. Anhydrous Phosphoric Acid, $P_2O_5=71{\cdot}465$.

This compound is formed only when phosphorus is burned in dry air or oxygen gas. It then appears as a white solid, like snow, which rapidly attracts moisture from the air, and passes into metaphosphoric acid, P_2O_5, HO, or P_2O_6, H; and this, again, soon changes, in contact with water, especially if heated, into common or hydrated phosphoric acid, $P_2O_5, 3\,HO$, or P_2O_8, H_3. The anhydrous phosphoric acid, like the anhydrous sulphuric acid, can hardly be said to be an acid body, as it does not exhibit acid properties until it has been brought into contact with water.

2. Hydrated Phosphoric Acid.

There are three different acids to which this name may be given. If we view them as compounds containing water, then they all contain anhydrous phosphoric acid, combined in each with a different proportion of water, and their formulæ will be P_2O_5, HO; $P_2O_5, 2\,HO$; and $P_2O_5, 3\,HO$. If, on the other hand, we view them as hydrogen acids, then they contain no anhydrous phosphoric acid, but are quite distinct compounds, and their formulæ will be as follows—P_2O_6, H; P_2O_7, H_2; and P_2O_8, H_3. The latter view is much more probable, and agrees better with the properties and composition of these acids, and of their salts. The first is called metaphosphoric acid, the second pyrophosphoric acid, and the third common phosphoric acid; or they may be still better designated as monobasic, bibasic, and tribasic phosphoric acids.

METAPHOSPHORIC, OR MONOBASIC PHOSPHORIC ACID.

P_2O_5, HO, or $P_2O_6, H = 80{\cdot}478$.

This acid is easily obtained by dissolving phosphorus in diluted nitric acid with the aid of heat, evaporating to a syrup, and exposing the residue to a red-heat in a platinum crucible. Or the solution of the anhydrous acid may be treated in the same manner; or phosphate of ammonia may be ignited in a platinum crucible. When phosphoric acid has once come in contact with water, it can never be rendered anhydrous by heat; it can only be reduced to the state of monobasic acid.

As thus obtained, it appears in the shape of a colourless and transparent glass, which slowly dissolves in water. It is hence called glacial phosphoric acid. Its solution causes in solutions of silver a white granular precipitate of monobasic phosphate of silver; it also coagulates albumen. But if long kept, or if very rapidly boiled, this solution passes into one of tribasic phosphoric acid, and no longer precipitates silver or coagulates albumen. Here 2 eqs. of water enter into the composition of the acid; $P_2O_5, HO + 2HO = P_2O_5, 3HO$.

With bases, this acid forms one series of salts, the monobasic phosphates, the general formula of which is P_2O_5, MO, or P_2O_6, M. In these, the hydrogen of the acid is replaced by its equivalent of metal. The precipitate caused by the acid in solutions of silver is one of these salts, P_2O_5, AgO.

PYROPHOSPHORIC, OR BIBASIC PHOSPHORIC ACID.

$P_2O_5, 2HO$, or $P_2O_7, H_2 = 89{\cdot}491$.

When common or tribasic phosphoric acid, $P_2O_5, 3HO$ is heated for some time to 417°, it loses one-third of the water it contains, and becomes bibasic, or pyrophosphoric acid. It appears as a viscid syrup, very acid, and very soluble in water. Its solution neither precipitates silver nor coagulates albumen; but if previously neutralised by ammonia it causes in salts of silver a flaky white precipitate of bibasic phosphate of silver, $P_2O_5, 2AgO$. The solution of this acid, like that of the preceding, soon passes into tribasic acid, especially if heated.

With bases it forms two series of salts, one containing 2 eqs. of base, the other 1 eq. of base, and 1 of water. The former are neutral, and have the general formula $P_2O_5, 2MO$: the latter are acid, and their formula is P_2O_5, MO, HO. This acid is much more easily obtained in combination with a base than in the free state, and in fact it was discovered in the salt obtained by igniting the common phosphate of soda, when there is left pyrophosphate or bibasic phosphate of soda, $P_2 O_5$, 2 Na O.

When a pyrophosphate is melted with excess of base, it is converted into a tribasic phosphate. Thus, if pyrophosphate of soda be fused with an additional equivalent of soda, the tribasic salt, $P_2 O_5$, 3 Na O is formed, which no longer contains pyrophosphoric acid.

COMMON, OR TRIBASIC PHOSPHORIC ACID.

$P_2 O_5$, 3 HO; or $P_2 O_8$, H_3=98·504.

When a solution of any of the preceding acids is evaporated by a moderate heat to the consistence of syrup, the residue is found to be the tribasic acid $P_2 O_5$, 3 HO. Heated for a long time to 417°, it loses 1 eq. water and becomes bibasic; heated to redness it gives off 2 eqs. water, and becomes monobasic. A diluted solution of either of these gradually becomes tribasic, and this change is very rapidly effected by boiling. Solution of common phosphoric acid neither precipitates silver nor coagulates albumen; but if neutralised by ammonia, it causes in salts of silver a pale yellow precipitate of tribasic phosphate of silver, $P_2 O_5$, 3 Ag O.

The most economical method of preparing phosphoric acid is to add to the syrupy superphosphate, or acid phosphate of lime, previously described, oil of vitriol as long as it causes a precipitation of sulphate of lime. The mixture becomes quite thick, and is to be diluted with water, filtered, again concentrated to a syrup, and again tested by adding a few drops of oil of vitriol. When no more sulphate of lime is formed, the solution is free from lime, but still contains phosphate of magnesia. It is to be evaporated and gradually heated to redness in a platinum vessel, by which means all the excess of sulphuric acid is expelled, and a glass is left. To separate the magnesia, this glass is to be dissolved in warm water, and the solution evaporated in a platinum dish till its temperature reaches 600° F. and phosphoric acid begins to be expelled along with the water. At this point the thick viscid mass becomes turbid, from the separation of insoluble phosphate of magnesia; and if the same temperature is kept up for a quarter or half an hour, the whole of the magnesia assumes the insoluble form. Water being now added, the pure phosphoric acid dissolves, the insoluble phosphate of magnesia is separated by filtration, and the filtered liquid is a pure solution of phosphoric acid. It is now evaporated and once more gently ignited in a covered platinum vessel. Pure monobasic phosphoric acid is left. It is now dissolved in hot water, and becomes tribasic acid, the form usually employed, as it is the most permanent. Like the other phosphoric acids, it is very acid, but not corrosive. It is occasionally used in medicine.

With bases, common phosphoric acid forms three series of salts, in which the 3 equivalents of water in the acid are wholly or partially replaced by metallic oxides. Thus, with soda it forms three salts; 1st, neutral phosphate $P_2 O_5, 3 Na O$; 2nd, common phosphate of soda, $P_2 O_5, 2 Na O, HO$; 3rd, acid phosphate of soda, $P_2 O_5, Na O, 2 HO$. In each of these salts there are 3 eqs. of base, but these may be either all soda, or partly soda and partly basic water. All three salts give with the salts of silver the same yellow precipitate, $P_2 O_5, 3 Ag O$; but the supernatant liquid is only neutral when the neutral phosphate is used; it is acid in the case of the other two salts, because, for every eq. of oxide of silver in the precipitate, 1 eq. of nitric acid has to be neutralised, and this cannot be effected by the basic water, but only by the soda.

When the second or common phosphate of soda is ignited, its basic water is driven off, and bibasic phosphate of soda $P_2 O_5, 2 Na O$, is left. This salt, dissolved in water, gives with salts of silver a white flaky precipitate of bibasic phosphate, while the supernatant liquid remains neutral.

If the third or acid phosphate of soda be ignited, it loses 2 eqs. of basic water, and monobasic phosphate is left, which, if dissolved in water, gives with silver a granular white precipitate of monobasic phosphate, the supernatant liquid remaining neutral.

From the above brief description of the three modifications of phosphoric acid, it will be seen that their characters are distinct and well marked. Graham views them, according to the formulæ which assume the presence of water, as three different hydrates of the same anhydrous acid; and he considers that when the anhydrous acid has combined with one, two, or three atoms of water, it acquires and retains, in each case, the power or tendency to combine with one, two, or three equivalents of fixed base. The facility with which one form passes into the other is in favour of this view; but it must be observed that it affords no explanation of the remarkable tendency alluded to, but only states the fact, and still leaves unanswered the question, Why does anhydrous phosphoric acid at one time unite with 1 eq., at another with 2 eqs. or 3 eqs. of water? or why does it, by doing so, acquire the tendency to unite with 1, 2, or 3 eqs. of base?

Liebig, on the other hand, considers the three acids as radically different, being formed of hydrogen, united in each to a different compound radical; and that as in the first there is only 1 eq., in the second 2 eqs., and in the third 3 eqs. of hydrogen, the salts must necessarily contain equivalent proportions of metals which, in the two latter, may replace the hydrogen either wholly or partially, as in other polybasic acids. The formulæ for the acids, on this view, have been given above.

The now-admitted existence of numerous polybasic acids, and the growing tendency to consider all hydrated acids as hydrogen acids, tend to induce us to prefer the latter view, which moreover has the advantage of at least offering an explanation of the different neutralising power of the three acids, which is referred to the amount of replaceable hydrogen they contain. Thus we have—

Monobasic Acid.		Bibasic Acid.		Tribasic Acid.	
Acid.	Salts.	Acid.	Salts.	Acid.	Salts.
P_2O_6, H;	$P_2\ O_6, M$;	P_2O_7, H_2;	$P_2\ O_7, M_2$;	P_2O_8, H_3;	P_2O_8, M_3;
			$P_2O_7 \left\{ \begin{matrix} M \\ H \end{matrix} \right.$		$P_2O_8 \left\{ \begin{matrix} M_2 \\ H \end{matrix} \right.$
					$P_2O_8 \left\{ \begin{matrix} M \\ H_2 \end{matrix} \right.$

If we begin from the tribasic acid, and represent one of its salts, the common phosphate of soda, $P_2\ O_8, \left\{ \begin{matrix} Na\ 2, \\ H, \end{matrix} \right.$ as follows;

$$P_2\,O_8 + \left\{ \begin{matrix} Na_2 \\ H \end{matrix} \right. = \left\{ \begin{matrix} \frac{1}{3}\,P_2\,O_8 + Na \\ \frac{1}{3}\,P_2\,O_8 + Na \\ \frac{1}{3}\,P_2\,O_8 + H \end{matrix} \right.$$

We see that when this salt is ignited, 1 eq. of hydrogen is expelled, along with 1 eq. of oxygen, and the 2 eqs. of sodium now neutralise the whole of the remaining phosphorus and oxygen, which is $\frac{3}{3}\,P_2\ O_8 - O = P_2\ O_7$, and the bibasic salt, $P_2\ O_7, Na_2$ results. If this be expressed by

$$P_2\,O_7 + Na_2 = \left\{ \begin{matrix} \frac{1}{2}\,P_2\,O_7 + Na \\ \frac{1}{2}\,P_2\,O_7 + Na \end{matrix} \right.$$

We see that something has been added to the radical previously united with each eq. of sodium, without altering its neutralising power. In like manner, if we represent microcosmic salt $P_2\,O_8, \left\{ \begin{matrix} Na \\ NH_4 \\ H \end{matrix} \right.$ as follows,

$$P_2\,O_8 + \left\{ \begin{matrix} Na \\ NH_4 \\ H \end{matrix} \right. = \left\{ \begin{matrix} \frac{1}{3}\,P_2\,O_8 + Na \\ \frac{1}{3}\,P_2\,O_8 + NH_4 \\ \frac{1}{3}\,P_2\,O_8 + H \end{matrix} \right.$$

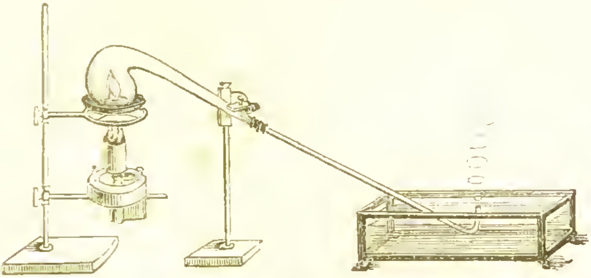
We see that when it is ignited, the hydrogen and the ammonium are both expelled, each combined with 1 eq. of oxyen; but as the rest of the phosphorus and oxygen formerly combined with them is not expelled, it enters into the composition of the radical still united with the 1 eq. of sodium, but without affecting its neutralising power. This radical, therefore, becomes $\frac{3}{3} P_2 O_8 - O_2 = P_2 O_6$; and its salt with sodium is $P_2 O_6$, Na, the monobasic phosphate of soda. If, now, we turn to what was said above of the acids of sulphur, viewed as hydrogen acids, we shall there see many analogous cases of the addition to the acid radical of different quantities of its elements, while the neutralising power remains unchanged. Thus, hdyrated sulphurous acid, $H + SO_3$, by the additon of $SO_3 + S_2$ to its radical, becomes the acid of Fordos and Gelis, without change of neutralising power. In the phosphoric acids, the neutralising power varies, because the hydrogen varies: but when they are represented, as has been done above, in such a way as to keep the hydrogen (or metal) the same in all, the analogy between them and the acids of sulphur, in regard to the non-dependence of the neutralising power on the nature and proportions of the ingredients of the radical, becomes manifest.

The above is the view which Liebig takes of the nature and formation of the three phosphoric acids. It must be admitted, that it has the advantage of simplicity; that it explains, in a consistent manner, all the known facts; and that it is at present better supported, and rests on fewer assumptions, than any other theory of the constitution either of these acids, or of acids in general.

PHOSPHORUS AND HYDROGEN.

Phosphuretted Hydrogen. $P_2H_3 = 34{\cdot}4$.

This compound may be formed by the action of phosphurets of alkaline metals on water, or by the action of phosphorus on boiling alkaline solutions. Thus, phosphuret of calcium, thrown into water, disengages the gas in question; and it is also produced in large quantity by applying heat to a mixture of lime, water, and fragments of phosphorus, in a retort nearly filled with the mixture, or by boiling phosphorus with an alcoholic solution of potash. The two former methods yield it in a form in which it is spontaneously combustible on coming in contact with air or oxygen; the latter in a form in which it requires the contact of flame in order to burn. The gas in both cases is essentially the same; but in the former it contains a minute proportion of a compound, not yet isolated, which is spontaneously inflammable, and which, inflaming by contact of air, kindles the gas. This compound is supposed to be P_2H_2. When the spontaneously inflammable gas is long kept, it deposits a solid compound, P_2H, and is then no longer spontaneously combustible. Possibly $2P_2H_2$ yield P_2H and P_2H_3.



The gas, whether spontaneously inflammable or not, is colourless, and has a very offensive smell of putrid fish. When it burns, it produces anhydrous phosphoric acid and water, forming thick white vapours; and when bubbles of the spontaneously inflammable gas take fire in still air, they form beautiful circular wreaths of vapour, which ascend, gradually widening, till they are dissipated in the air.

The addition of ether, oil of turpentine, and many other substances, destroys the spontaneous inflammability; but this property may be restored by adding to the gas a minute proportion of nitrous acid.—(Graham.)

Phosphuretted hydrogen is neither acid nor alkaline; but it seems to have alkaline tendencies, since it combines with hydriodic acid, forming a neutral crystalline compound, isomorphous with hydriodate of ammonia. It also combines with several metallic chlorides, forming compounds analogous to those produced by ammonia with the same chlorides. Rose, who has described these compounds, points out a considerable analogy between phosphuretted hydrogen and ammonia.

It has already been mentioned, that when hypophosphorous and phosphorous acids are heated, they are resolved into phosphoric acid and phosphuretted hydrogen. This gas is consequently given off frequently towards the end of the evaporation of a solution of phosphorous in diluted nitric acid, which at first forms phosphorous acid, by the decomposition of which the gas is produced, causing a sudden combustion at the surface of the evaporating liquid.

Since the above account was printed, M. P. Thénard has published an elaborate Memoir on phosphuretted hydrogen, from which it appears that there exist 1st, a fluid compound P_2H_2 or $5\,P_2H_2 = P_{10}H_{10}$: 2nd, a solid compound P_4H; and 3rd, the gas P_2H_3. The fluid is first formed, and is then spontaneously or very easily resolved into the other two. Thus—

$$P_{10}H_{10} = P_4H + 3\,P_2H_3.$$

The gas, P_2H_3, acquires its spontaneous combustibility by dissolving some of the liquid PH or $P_{10}H_{10}$. In fact this liquid communicates the same property to other gases.

PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen. $NP_2 = 45{\cdot}52$.

This is a white insoluble powder, formed by the action of ammonia on sesquichloride of phosphorus. $NH_3 + P_2Cl_3 = 3\,HCl + NP_2$. It is infusible and fixed in the fire in close vessels.

PHOSPHORUS AND CHLORINE.

Phosphorus takes fire spontaneously in chlorine gas, forming two compounds.

a. Sesquichloride of Phosphorus. $P_2Cl_3 = 137{\cdot}81$.

When phosphorus is made to pass, in the form of vapour, through a tube filled with coarse powder of bichloride of mercury, $HgCl_2$, or when chlorine is slowly passed through a tube or retort containing phosphorus, a volatile colourless liquid is obtained, which is sesquichloride of phosphorus. $3\,HgCl_2 + P_2 = 3\,HgCl + P_2Cl_3$. Here protochloride of mercury is left, while the excess of chlorine combines with the phosphorus. The sesquichloride is a pungent fuming liquid, which, in contact with water, yields hydrochloric and phosphorous acids. $P_2Cl_3 + 3\,HO = 3\,HCl + P_2O_3$.

b. Perchloride of Phosphorus. $P_2Cl_5 = 208{\cdot}75$.

This compound is best formed by passing a current of chlorine through the preceding to saturation. It is a white volatile solid, of a pungent smell. In contact with water, it yields hydrochloric and phosphoric acids: $P_2Cl_5 + 5\,HO = 5\,HCl + P_2O_5$.

PHOSPHORUS AND BROMINE.—PHOSPHORUS AND IODINE.

With these elements, phosphorus also unites with spontaneous combustion, and forms with each two compounds, analogous to those with chlorine. They are volatile solids, yellow in the case of bromine, dark brown or nearly black in the case of iodine. They decompose water like the chloride, with the production of hydrobromic and hydriodic acids on the one hand, and phosphorous or phosphoric acids on the other.

PHOSPHORUS AND SULPHUR.

When phosphorus and sulphur are heated together under water they combine, often with incandescence, forming several compounds, which are exceedingly inflammable, and having a tendency to explode violently when heated, from some unknown cause, are very dangerous to experiment with. Berzelius has lately examined these compounds, and has described the following. 1. P_4+S. This compound occurs in two states, as a colourless liquid, and as a red powder; 2. P_2S. A pale yellow liquid, also as an orange powder; 3. P_2S_{12}. Yellow crystals; 4. $P_6S_2 = P_4S + P_2S$. A scarlet powder, changed by distillation into a liquid; 5. P_2S_3. A yellow fusible solid; 6. P_2S_5. A yellow crystallisable solid.—It is very remarkable, that several of these compounds occur in two distinct states; and Berzelius conceives that this is owing to the circumstance that, like sulphur, phosphorus itself exists in two mechanically distinct states, and that the difference of the two states of the compounds depends on the one containing phosphorus in its ordinary condition, while in the other the phosphorus is in the allotropic state, as it is now called.

In the above section, we have considered the atom of phosphorus to be 15·7, on which view most of the compounds of phosphorus must contain 2 atoms and 1 equivalent. Thus phosphoric acid is P_2O_5, phosphorous acid P_2O_3; phosphuretted hydrogen P_2H_3: the chlorides of phosphorus P_2Cl_3, and P_2Cl_5. But since that section was first printed, the continental chemists have, for the most part, adopted the equivalent of hydrogen generally admitted in this country; as well as the view, according to which atom and equivalent are synonymous, or at least convertible terms. It is on this account that they now admit our atomic weight of hydrogen: and to be consistent we should apply the same rule to phosphorus, which, as we have seen, enters into combination nearly if not altogether uniformly, in the proportion of two atoms. In fact we do admit the equivalent of phosphorus to be 31·4. Now it appears to me that we ought to call this not only one equivalent, but also one atom. In that case, phosphoric acid will be $P O_5$, phosphorous acid, $P O_3$, phosphuretted hydrogen, (liquid) $P H_2$: (solid) P_2H ; and gaseous, PH_3 ; and the chlorides of phosphorus $P Cl_3$ and $P Cl_5$.

The same change ought to be adopted in the case of arsenic, the atom of which, instead of 37·7, ought to be 75·4, and the formulæ of arsenious and arsenic acids, instead of $As_2 O_3$ and $As_2 O_5$, will be $As O_3$ and $As O_5$.

It is possible that some other atomic weights will have to be doubled in the same way. Those of iron and chromium, however, although these elements form compounds such as $Fe_2 O_3$, $Fe_2 Cl_3$, $Cr_2 O_3$, $Cr_2 Cl_3$ &c., &c., do not require this change, because these metals also form compounds such as $Fe O$, $Fe Cl$, $Fe S$, $Cr O_3$ &c., &c.

The reader can easily make for himself the necessary alterations on the tables, formulæ and equations, where phosphorus and arsenic occur.

11. Carbon. $C = 6·04$.

This element occurs very abundantly in nature, generally combined. In the pure state, and crystallised, it constitutes the diamond. In a compact, amorphous condition, it occurs as plumbago or graphite ; and in a much less pure form as anthracite coal. It is an essential ingredient of all organised tissues and products, animal and vegetable; and it is also found in the mineral kingdom as the chief component of pit coal and wood coal, which are evidently derived from vegetables ; and, further, as carburetted hydrogen gas, the fire-damp, and carbonic acid gas, the choke-damp of coal mines, which are products of the decay of vegetable matter. Carbonic acid is abundant in volcanic districts and in mineral waters, and, combined with lime or magnesia,. constitutes extensive rock formations. Carbonate of lime occurs, for example, as marble, limestone, and chalk ; and along with carbonate of magnesia as dolomite. When crystallised, it forms calcareous spar. Carbonate of magnesia also forms rocks in some parts of the world. In smaller quantity, the carbonates of baryta, strontia, lead, and some other bases, are also found. Carbonic acid gas is always present in the atmosphere, of which it forms about $\frac{1}{1000}$ by weight.

Carbon is artificially prepared by heating organic matter in close vessels as long as any volatile substances are given off. These volatile bodies are compounds of carbon, hydrogen, nitrogen, and oxygen, in various proportions, and the residue is the excess of carbon, which is fixed in the fire, provided oxygen be excluded. Wood thus treated yields common charcoal, which is carbon + the ashes or mineral elements of the wood. Coal yields coke, which is more dense in its structure. Animal matters yield animal charcoal, which contains phosphates, and also nitrogen, probably as mellone, $C_6 N_4$. The charcoal from bones is called bone or ivory black, and is of course loaded with phosphate of lime. When oils or resins, which are always rich in carbon, are burned with a deficient supply of oxygen, they yield a great deal of soot, which is called lamp-black. When ignited in close vessels, to expel any traces of oil or volatile matters, it is almost pure carbon.

The diamond, or crystallised carbon, is the hardest body known. Its Sp. G. is 3·5. It is also quite infusible, but is easily burned when heated in oxygen, and is converted into carbonic acid. It is remarkable for its transparency and high refractive and dispersive power: it is a non-conductor of electricity. In the other (allotropic ?) form of graphite, anthracite, or charcoal, carbon is opaque, black, combustible in air or oxygen, yielding carbonic acid, but is now a conductor of electricity. Its Sp. G. is 2. In all its forms, carbon is devoid of taste or smell, insoluble, as such, in all menstrua (although it may be oxidised and dissolved as carbonic acid by strong nitric acid, or aqua regia, with the aid of heat), and altogether fixed in the fire in close vessels.

In open vessels, carbon, when heated, takes fire, and, if pure, burns entirely away, being converted into carbonic acid gas. Indeed, the attraction of carbon for oxygen at a red-heat exceeds that of almost all other bodies. It is to this property, and to the heat and light given out in its combustion, that are owing the uses of carbon, as the chief ingredient of all kinds of fuel, whether burned for heat or for light.

CARBON AND OXYGEN.

With oxygen, carbon forms two well-marked gaseous compounds, which shall be here described. The same elements, in other proportions, constitute, according to the opinion which regards oxygen acids as hydrates, certain anhydrous acids, to be described under the head of organic chemistry. As these anhydrous acids, however, are not known in the separate form, we may rather consider the acids in question (the oxalic, mellitic, croconic, and rhodizonic acids) as compounds of hydrogen.

a. Carbonic Oxide. $CO = 14{\cdot}053$.

This gas is formed either when carbon is burned with a limited supply of air, as when air is passed through a mass of red-hot charcoal; or when carbonic acid is brought into contact with red-hot charcoal. In the latter case, the carbonic acid, CO_2, is deoxidised, while the carbon is oxidised, $CO_2 + C = 2\,CO$.

It is best obtained by heating in a retort 1 part of finely-powdered ferrocyanide of potassium (prussiate of potash) along with 10 parts of oil of vitriol. The salt contains cyanide of potassium, $K, C_2 N$, and cyanide of iron, $Fe, C_2 N$. One or both of these salts acts on the sulphuric acid and water, yielding sulphate of potash (or of iron), sulphate of ammonia, and carbonic oxide, $K, C_2 N + 2\,(HO, SO_3) + 2\,HO = (KO, SO_3) + (NH_4 O, SO_3) + 2\,CO$. The gas may also be obtained by heating a mixture of a formiate, $MO, C_2 HO_3$, with an excess of oil of vitriol, $MO, C_2 HO_3 + HO, SO_3 = MO, SO_3 + 2\,HO + 2\,CO$. When oxalic acid, $HO, C_2 O_3$, or an oxalate, $MO, C_2 O_3$, is heated with an excess of oil of vitriol, there is obtained a mixture of carbonic oxide and carbonic acid gases, $MO, C_2 O_3 + HO, SO_3 = MO, SO_3 + HO + CO + CO_2$. By passing the mixed gases through milk of lime, or solution of potash, the carbonic acid is arrested, and the carbonic oxide gas obtained pure.

Carbonic oxide gas may be collected and kept over water. It is transparent and colourless, has neither taste or smell, and when respired is fatal to animal life. It takes fire when heated to redness in contact with air, as by the approach of a candle, and burns with a lambent clear blue flame, combining with a second equivalent of oxygen, and yielding carbonic acid. Its Sp. G. is 0·9722. The blue flame that is often seen to play on the surface of a large red-hot coal fire is owing to the formation of this gas; the carbonic acid formed at the lower part of the fire being forced to pass through a thick mass of red-hot charcoal. The formation of this poisonous gas is also one cause of the danger of slowly burning charcoal in chauffers, in rooms where there is no chimney and little ventilation.

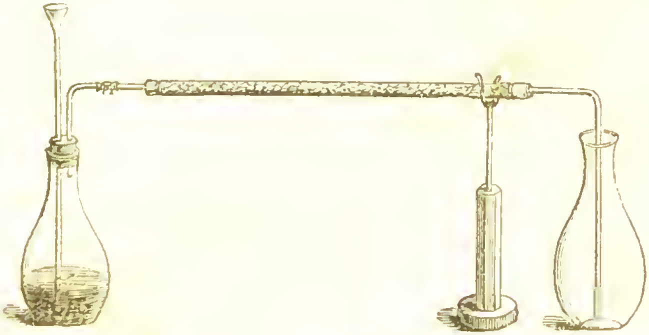
Carbonic oxide is a compound radical; that is, it acts like an element, combining with elements. Thus, it combines with chlorine, with oxygen, with metals. In this point of view it is a most interesting compound; but, like cyanogen, comes to be treated of as a compound radical in the organic division of this work.

b. Carbonic Acid. $CO_2 = 22$.

SYN. *Fixed Air.*—This gas occurs in a variety of circumstances, which have been noticed above, in treating of carbon. In addition to these, it may here be mentioned that it is formed during the respiration of animals, and that it is a chief product of the vinous or alcoholic fermentation. It is also formed in large quantity in all ordinary combustions, from the oxidation of the carbon in the fuel.

It is best prepared artificially by the action of diluted hydrochloric or sulphuric acid on marble or chalk, which, as already stated, is carbonate of lime, CaO, CO_2. Thus we have $CaO, CO_2 + HCl = CaCl + HO + CO_2$. It may be collected, with some loss, over water, which absorbs it to a considerable extent.

It is a transparent and colourless gas, with a rather pungent, subacid smell, and a slight acidulous taste. Its Sp. G. is 1·527; and it is so much heavier than air, that it may be collected in vessels by displacement, as represented in the cut, especially if it be wanted dry, after passing through a tube filled with chloride of calcium. Lime water is rendered turbid by this gas, the insoluble carbonate of lime being formed; and by this character it is distinguished from all other gases. It extinguishes flame, and is most deleterious when inhaled. As it is apt, from its great density, to accumulate in the lower part of wells, pits, or mines, where it escapes, it is often the cause of fatal accidents. No such place should be entered until a light has been introduced, and found to burn brightly; if it burns dimly, or is extinguished, the air will certainly destroy life if respired.



Carbonic acid gas, by a pressure of 36 atmospheres, is liquefied. This is best accomplished by condensing the gas, by means of a pump, into a strong copper vessel, such as is used for air-guns. The liquid carbonic acid, by its almost instantaneous evaporation, when allowed to escape through a jet, produces so much cold as to freeze a part of the gas into a white solid like snow. The solid carbonic acid evaporates slowly, but, if mixed with ether, more rapidly, so as to freeze mercury easily. The liquid acid expands by heat in a greater degree than even the gas does.

Carbonic acid gas is absorbed by water, particularly under increased pressure, and gives to that liquid an acidulous taste and the power of reddening litmus ; although, on exposure to the air, or on boiling, the gas is given off, and the blue colour is restored. With the bases, it unites, forming salts, which are called carbonates ; but in the soluble carbonates the alkali is not neutralised, and many carbonates of the base, especially of ammonia, may be obtained, in all of which the properties of the alkali predominate. It would appear, from this, that carbonic acid is not a true acid, although it combines with bases. We shall hereafter see that one or two other oxygen acids which, like it, do not form hydrates, are, in like manner, destitute of the true character of acids.

The sparkling and effervescing properties of many kinds of wine, of beer, and of soda water, is owing to the presence of carbonic acid. The mineral waters, in which it occurs free, are known by their sparkling, and are much used.

CARBON AND HYDROGEN.

These two elements combine together in a vast number of proportions, and being both combustible, give rise to compounds, all of which are highly inflammable, and which resemble each other in chemical characters generally. They are often called carbo-hydrogens. At the ordinary temperature, some are solid, as paraffine and naphthaline ; many are liquid, as oils of turpentine and lemons, naphtha, &c. ; and two are gaseous, namely, light carburetted hydrogen gas, and olefiant gas. All of these compounds are either vegetable products, or arise from the decay or the destructive distillation of organic matter. As, however, the two gases, mixed in various proportions with air, constitute the fire-damp of coal mines, and consequently occur in the mineral kingdom, we shall describe them here, leaving the remainder for organic chemistry.

a. Light Carburetted Hydrogen, $CH_2 = 8{\cdot}04$.

This gas forms the chief part of the combustible gases, which issuing from the seams in the coal, mixes with the air of the mines, and produces the explosive fire-damp. It is produced nearly pure, when vegetable matter decays under stagnant water. The bubbles which rise are found to consist of this gas, with a little carbonic acid, which may be removed by solution of potash. The gas may also be formed artificially by heating an acetate, $MO, C_4H_3O_3$, with an excess of hydrate of baryta. We have then

$$(MO + C_4H_3O_3,) + BaO, HO = MO, CO_2 + BaO, CO_2 + 2\,CH_2.)$$

The gas is colourless and inflammable, burning with a yellowish flame, and forming carbonic acid and water with the oxygen of the air. $CH_2 + O_4 = CO_2 + 2\,HO$. Its Sp. G. is 0.5555. When mixed with twice its volume of oxygen and set fire to, it explodes violently. The same result follows, but with less violence, when it is mixed with 10 vol. of air, which contains 2 vols. oxygen. This is the nature of fire-damp. It is a mixture of this gas with air. If the air is less than 6 times, or more than fourteen times the volume of the gas, explosion does not take place.

To put an end to the frightful accidents formerly so common in coal-mines, Davy invented his safety-lamp, which is only a common oil-lamp, surrounded by wire gauze. Davy found that flame, which is incandescent gaseous matter, and intensely hot, could not pass through fine wire gauze, the gaseous matter being cooled by the contact with the metal, below the point at which it becomes luminous. Now, as it requires the heat of flame to fire the explosive mixture, it is evident that the flame of the lamp, not being able to pass through the wire-gauze as flame, but only as gaseous matter not incandescent, cannot fire the mixture which surrounds it. Since this beautiful contrivance was adopted, explosions have become much more rare in coal-mines; and there is good reason to believe that such as have occurred, have arisen from neglect of the use of the safety-lamp, or from carelessness in using lamps, the gauze of which has been so injured by blows, or otherwise, as to allow the flame to pass.

When an explosion takes place, those who are not burnt or shattered, are generally suffocated by the carbonic acid, which is the product of the explosion.

b. Olefiant Gas. $C_2H_2 = 14{\cdot}08$; or, $C_4H_4 = 28{\cdot}16$.

This gas occurs in the gaseous mixture of coal-mines, mixed with the preceding. It is prepared by heating 1 part of strong alcohol with 4 parts of oil of vitriol. The mixture blackens and gives off the gas, which may be collected over water. It is rendered quite pure by passing it through oil of vitriol, which removes some of the vapour of ether which is generally present.

Olefiant gas is transparent and colourless. When brought in contact with a flame in the air, it takes fire, and burns with a very luminous white flame. Mixed with its volume of chlorine, the two gases rapidly disappear, producing an ethereal or oily liquid, $C_4H_4Cl_2$; hence the name. But if mixed with 2 vols. of chlorine, and set fire to, the mixture burns off with a red flame, and an immense quantity of smoke, which is carbon deposited in the solid form, the hydrogen uniting with the chlorine. $C_2H_2 + Cl_2 = 2\,HCl + C_2$.

When a light is applied to a mixture of 1 vol. of olefiant gas, and 3 vols. of oxygen, or 15 vols. of air, a very violent explosion takes place, the products being carbonic acid and water. $C_2H_2 + O_6 = 2\,HO + 2\,CO_2$.

CARBON AND NITROGEN.

Cyanogen. $C_2N = Cy = 26{\cdot}23$.

These elements in the nascent state, and in the presence of a base, combine to form a very remarkable compound, which, from being a chief ingredient in Prussian blue, has been called Cyanogen. This compound is best obtained by heating a mixture of 6 parts of dried ferrocyanide of potassium, and 9 parts of bichloride of mercury in a flask, when cyanogen is given off in the form of a colourless gas, absorbed by water, having a very pungent and peculiar smell. Cyanogen gas is combustible, and burns with a beautiful purplish red flame. It is liquefied by a pressure of 3 or 4 atmospheres.

Such are the leading external properties of this remarkable compound, which, in its chemical relations, however, acts most frequently the part of a simple acid radical, entirely analogous to chlorine, bromine, iodine, or fluorine, forming an acid with hydrogen, and neutral salts with metals.

In fact, cyanogen is the type of the important class of compound acid radicals, which characterise the chemistry of organic bodies, although, as we have seen, they also occur in inorganic chemistry. But as cyanogen is exclusively a product of organised compounds, or of the destruction of organic bodies, the detailed description of its chemical relations, and of its numerous compounds, belongs to organic chemistry.

The composition of cyanogen is $C_2 N$; but as it plays the part of an elementary body, it is generally more convenient to employ for it the symbol Cy.

Carbon and nitrogen form another compound, $C_6 N_4$, which is also a compound radical, and is called Mellone. Symbol, Me.

CARBON AND CHLORINE.

Carbon does not directly unite with chlorine; but when chlorine is made to act on certain organic compounds, which are decomposed by it, the carbon being presented to it in the nascent state, combines with the chlorine. There are several chlorides of carbon: 1. Dichloride of carbon $C_2 Cl$, a white solid fusible and combustible body. 2. Protochloride of carbon, C Cl, a liquid, boiling at 160°. 3. Perchloride of carbon, $C_2 Cl_3$, a very fusible solid, boiling at 360°, combustible. None of these compounds have any practical interest.

Little, if anything, is known of the compounds of iodine, bromine, and fluorine, with carbon.

CARBON AND SULPHUR.

Bisulphuret of Carbon, $CS_2 = 38{\cdot}28$.

This compound is best formed by filling with fragments of recently ignited charcoal a wide cast-iron tube, which is placed in a somewhat inclined position across a furnace. The lower end of the tube is connected with Liebig's condensing apparatus, the wide glass tube of which is kept cold by iced water, and terminates in a two-necked bottle, also placed in ice-cold water; a tube in the second tubulature of the bottle, allows the escape of gaseous matter. The part of the iron tube containing the charcoal being now raised to a red-heat, a fragment of sulphur is introduced into the upper end, which is instantly closed. The sulphur melts, boils, and passes in vapour over the hot charcoal, which combines with it, forming bisulphuret of carbon, which condenses in the bottle as a volatile liquid. A second fragment of sulphur is introduced very soon after the first; and if the proportion of sulphur introduced at once, and the heat of the charcoal be fortunately observed, a large quantity of the new compound may soon be obtained. The gases disengaged appear to be a gaseons sulphuret of carbon, chiefly formed when there is too little sulphur, and sulphuretted hydrogen, arising from the presence of hydrogen or water in the charcoal.

The bisulphuret of carbon is purified by distillation in a very gentle heat, and then forms a very transparent, mobile, colourless liquid, of Sp. G. 1·272, sinking, therefore, in water, which has a peculiarly offensive smell of putrid cabbage. It is very volatile, boiling at 108°; and very combustible, burning with a pale blue flame, and producing sulphurous and carbonic acids. It is insoluble in water, soluble in alcohol, ether, and oils. It dissolves sulphur and phosphorus readily; and these solutions, by spontaneous evaporation, yield fine crystals of those elements. It also dissolves camphor, essential oils, and resins.

Sulphuret of carbon is occasionally used as an external application in burns; and it promises to be useful as a solvent for resins, many of which it dissolves readily, and thus forms varnishes, which, from its great volatility, dry very rapidly.

12. BORON. $B = 10·9$.

This element is found, in combination with oxygen, forming boracic acid in certain hot springs in the north of Italy; and as borate of soda (borax), on the shores of some lakes in Thibet.

From boracic acid, boron is with difficulty obtained by the action of potassium, aided by heat, which removes the oxygen. Or it may be prepared by the action of potassium on borofluoride of potassium, when boron is separated. $KF, BF_3 + K_3 = 4KF + B$. The fluoride of potassium which is formed, is dissolved away by water, and the boron remains as a dark olive-coloured powder. Boron is fixed in the fire, but if heated in oxygen gas it burns brilliantly, being converted into boracic acid.

Boron and Oxygen. Boracic Acid, $BO_3 = 34·939$.

When boron is heated in air it burns like tinder, or as above stated, if heated in oxygen, with a brilliant light, and yields this acid. It is obtained by evaporating the hot springs of Sasso, in Italy, in a somewhat impure state, under the name of Sassoline, or crude boracic acid. It is best prepared by dissolving borax in four parts of hot water, and adding to the hot solution one-third of the weight of the borax of oil of vitriol. Borax is a borate of soda; the sulphuric acid takes the soda, forming a soluble salt, and the boracic acid is set free. Being very sparingly soluble in cold water, it is deposited, on cooling, in scaly crystals, which are a crystallised hydrate of boracic acid, $BO_3 + 3HO$. These crystals are purified by being dissolved in the smallest possible quantity of boiling water after they have been washed with a little cold water. On cooling, this solution deposits pure hydrated boracic acid.

When the crystals are heated to 212°, they lose half the water they contain, and this is probably water of crystallisation. The residue is $2\,BO_3+3\,HO$; so that the original crystals may be represented as $2BO_3+3\,HO+3$ aq. When heated to redness the acid melts, and, on cooling, forms a transparent brittle glass. It is quite fixed in the fire in close vessels if dry; but it volatilises readily with the vapour of water, so that a solution of boracic acid cannot be evaporated without notable loss. It is in this way, along with steam, that it is brought from great depths into the springs in which it is found.

Boracic acid is sparingly soluble in cold, readily in hot water. It is very soluble in alcohol, and its alcoholic solution burns with a flame mixed and tinged with pale green: a property characteristic of the compounds of boron.

It is a feeble acid, and reddens litmus slightly: it colours turmeric brown, like alkali. With bases it forms salts called borates, which are for the most part insoluble. The alkaline borates alone are soluble. All the salts of this acid are very fusible, and promote the fusion of other bodies when mixed with them. Hence, borax is much used as a blowpipe flux, which not only promotes fusibility, but at a red-heat dissolves siliceous compounds to a clear, fusible glass.

No compounds are known of boron with hydrogen or nitrogen.

With chlorine boron combines when it is heated in the gas, or when chlorine is passed over a red-hot mixture of boracic acid and charcoal. The terchloride of boron, BCl_3, is a gas at ordinary temperatures. It has a pungent acid smell, and forms thick vapours in the air. These are the results of its action on the water of the atmosphere, whereby hydrochloric and boracic acids are formed: $BCl_3+3\,HO=3\,HCl+BO_3$.

Nothing is known of the compounds of boron with bromine and iodine.

BORON AND FLUORINE.

Terfluoride of Boron. $BF_3=66.94$.

Boron has a remarkable affinity for fluorine, and when fluor spar (fluoride of calcium) is heated to redness with boracic acid, a gaseous compound is produced, analogous in composition and properties to the terchloride of boron. $3\,Ca\,F+4$

$BO_3 = 3(CaO, BO_3) + BF_3$. The Sp. G. of the gas is 2·36. It instantly seizes on water, decomposing it, and thus, like the chloride, forms very thick vapours with the moisture of the air. It is, in fact, a very delicate test of the presence of moisture in any gas.

When this gas is absorbed by water to saturation, hydrofluoric acid and boracic acid are formed: $BF_3 + 3HO = 3HF + BO_3$. The hydrofluoric acid unites with the boracic acid and 1 eq. of water, forming an acid, $3HF + HO, BO_3$, and this, when acted on by bases, yields salts, the formula of which is $3MF + MO, BO_3$. Berzelius has shown that when terfluoride of boron is absorbed by concentrated hydrofluoric acid, another compound is formed, the formula of which is $HF + BF_3$. It is an acid, the formula of its salts being $MF + BF_3$. All its salts, when heated, give off terfluoride of boron.

Boron, when heated in the vapour of sulphur, burns and forms a sulphuret of boron, which is a white solid decomposed by water, with which it yields sulphuretted hydrogen and boracic acid.

13. Silicon. $Si = 22{\cdot}18$.

This element is, with the exception probably of oxygen, the most abundant of all those which form the solid mass of our earth. It occurs, however, only in a state of combination with oxygen, as silicic acid or silica, which is the chief ingredient of all rocks, except limestone, rock salt, and coal, and also of all soils.

Silicon is best obtained by heating potassium with silicofluoride of potassium, $3KF + 2SiF_3$, which with 6 eqs. of potassium yields $9KF + Si_2$. Water dissolves off the fluoride of potassium, and leaves the silicon as a dark brown powder, which contains some hydrogen, and is purified by exposure to a low red-heat. Silicon is infusible, and after having been ignited in close vessels it is so compact as not to burn when heated even in oxygen. It is not acted on by any acid except the hydrofluoric acid, which slowly dissolves it. A mixture of hydrofluoric and nitric acids acts more strongly. When silicon is fused with nitrate or carbonate of potash, it is oxidised with a smart deflagration. It is heavier than oil of vitriol.

SILICON AND OXYGEN.

Silicic Acid. $SiO_3 = 46{\cdot}219$.

Syn. *Silica.*—This acid is found pure in rock crystal, or in white quartz. Along with small and variable quantities of certain metallic oxides it forms many well-known minerals—as yellow or smoke rock crystal with oxide of iron; agate, jasper, heliotrope, carnelian, with the same metal; amethyst with oxide of manganese; prase with oxide of nickel; rose-quartz with some fugitive colouring matter; opal and calcedony with water, &c. &c. Many sands and sandstones are nearly pure silica, and quartz rock and flint are quite pure.

Silicic acid may be obtained in a state of purity, from any siliceous sand, by fusing it with three or four parts of carbonate of potash, dissolving the fused mass in water, adding hydrochloric acid, which separates the silica as a jelly, which is a hydrate of the acid, and evaporating the whole to dryness. Water removes from the dry mass all soluble chlorides, and leaves the silica, which, when dried, is a snow-white powder, insoluble in water, and all acids except the hydrofluoric acid. It dissolves in caustic or even carbonated alkalies with the aid of heat.

Silicic acid combines with bases, forming silicates, all of which, except those containing an excess of the stronger alkalies, are insoluble in water. The greater number of rocks and minerals consist of silicates, especially those of alumina, lime, magnesia, oxide of iron, potash, and soda. The silicates of potash and soda, when heated to redness, form glass, which when the acid predominates is insoluble, and is the basis of all ordinary glass; when the alkali is in excess, the glass is very soluble in water. Many silicates found in nature, as the zeolites, are soluble in strong acids; but most of them lose their solubility on being ignited. Many, such as felspar, are not attacked by acids, even before ignition.

No compounds are known of silicon with hydrogen or nitrogen.

SILICON WITH CHLORINE AND BROMINE.

When silicon is heated in chlorine it burns and forms a compound, which is better prepared by passing chlorine over a red-hot mixture of silicic acid and charcoal, $Si\,O_3 + C_3 + Cl_3 = Si\,Cl_3 + 3\,CO$. The compound, which is called terchloride of silicon, condenses in the cold part of the apparatus as a very volatile, pungent, and colourless liquid, which decomposes water, forming hydrochloric and silicic acids: $Si\,Cl_3 + 3\,H\,O = 3\,H\,Cl + Si,\,O_3$.

Bromine yields an analogous terbromide, $Si\,Br_3$, the properties of which are similar to those of the terchloride.

Iodine is not known to combine with silicon.

Silicon and Fluorine. $Si F_3 = 78.22$.

Silicic acid is rapidly dissolved by hydrofluoric acid, and a gas is produced, which is found to be a terfluoride of silicon: $Si O_3 + 3 H F = 3 H O + Si F_3$. This gas is best obtained by heating a mixture of powdered fluor spar and quartz with oil of vitriol: $3 Ca F + Si O_3 + 3 (H O, S O_3) = 3 (Ca O, S O_3) + 3 H O + Si F_3$. The gas must be collected over mercury. It is colourless, fuming strongly in the air, its Sp. G. 3·66. It is absorbed by water, and hydrated silicic acid is deposited, while an acid is found in the water composed of $3 HF + 2 Si F_3$. With bases this acid forms salts, called silicofluorides, the formula of which is $3 M F + 2 Si F_3$. These salts are nearly all insoluble, and when heated give off terfluoride of silicon.

The aqueous hydrofluosilicic acid is used in chemistry to separate potash, with which it forms an insoluble salt, from certain acids, such as chloric acid, by which means these acids are obtained in the free state. It is also used as a test, to distinguish between compounds of barium and of strontium, as it forms after a short time a crystalline deposit in the solutions of the former base only.

Heated with sulphur, silicon combines with it, forming a white earthy compound, $Si S_3$. It decomposes water, yielding sulphuretted hydrogen and silicic acid: $Si S_3 + 3 H O = 3 H S + Si O_3$.

METALS.

General Observations on Metals.

In the arrangement we have adopted, all the elements not hitherto described are considered metals, although some of them, especially arsenic and tellurium, are, in many points, very analogous to the metalloids. The metals are 42 in number, exclusive of the three lately announced by Mosander, the two announced by Rose, and one discovered by Klaus, which, if established, will raise the number to 48. See the list of elements, page 2.

A metal is defined to be a body possessing the peculiar appearance called the metallic lustre (which is well illustrated in polished silver or in mercury), and capable of conducting well both heat and electricity. All the metals possess this combination of characters, but in other physical characters they exhibit great variety. We shall notice the following:—Specific Gravity, Hardness, Tenacity, Fusibility, and Volatility.

1. Specific Gravity. The density of metals varies from 0·865

(water being = 1) to 21: the former being the Sp. G. of potassium, the latter that of platinum. Iridium is said to be still denser than platinum.

2. Hardness. Some metals, as potassium, lead, tin, silver, &c., are so soft as to be easily cut with a knife; potassium and sodium may even be kneaded in the fingers. Others, such as iron, nickel, antimony, &c., are much harder; and a few, such as rhodium and iridium, especially the latter, possess a very high degree of hardness.

3. Tenacity. This property is present in very various degrees in metals. Some, as antimony, bismuth, cobalt, have so little tenacity that they are brittle and may be powdered: while others may be beat out into thin leaves, or drawn into fine wires. Those two forms of tenacity, malleability and ductility, are not always proportional to one another; for iron, which can only be beat into plates of a very moderate thinness, being, of all the malleable metals, the least malleable, may be drawn out into very fine wires, and is among the most ductile of metals. Of the malleable metals, the following are remarkable: lead, tin, copper, palladium, platinum, silver, and gold. The last-named metal may be beat out into leaf so fine, that, although quite entire and free from visible pores, 57 square inches of the finest gold leaf will not weigh more than 1 grain. Zinc, which is rather brittle at ordinary temperatures, admits of being rolled into thin plates at 300° and 400°. The most ductile metals are lead, copper, palladium, iron, silver, gold, and platinum. 1 grain of gold may be drawn out into a wire 550 feet long, and platinum is about 6 times more ductile, according to Wollaston. Iron wire, although not the finest, is stronger than wire of equal diameter of any other metal.

4. Fusibility. One metal, mercury, is liquid at all temperatures above—39° F., and below 660°. Some, such as potassium, sodium, &c., melt at a very moderate heat: others, such as lead, tin, &c., at temperatures below red-heat; others at a strong red or white heat, such as copper, silver, and gold. Some, as platinum, rhodium, &c., require the heat of the oxygen and hydrogen blow-pipe to melt them; and one at least, iridium, appears to resist, when pure, even this intense heat.

5. Volatility. Some metals are very volatile compared with others. Mercury volatilises slowly at all temperatures above 80° or 100° F., and below its boiling point, at which temperature, 662°, it is rapidly converted into vapour. At the other extreme is iridium, which is quite fixed, not even melting in the strongest white heat yet known. The following metals are converted into vapour, or they boil, at temperatures varying from a low to

a bright red-heat: cadmium, zinc, arsenic, tellurium, potassium, and sodium. Most of the others are fixed, although some of them, in the flame of the oxy-hydrogen blow-pipe, appear to be volatilised in small quantity.

The chemical relations of metals are very important; and as there runs through the whole class a great analogy in this respect, it is advisable to describe, generally, the chemical characters of metals; by which means we are enabled to render the account of the individual metals more brief and more easily remembered.

Metals have powerful affinities, especially for the metalloids, with almost all of which they combine, and frequently in several proportions. In addition, therefore, to the important uses of the metals, as such, the useful applications of a large number of metallic compounds are of the highest interest and value.

Almost all the metals have a powerful affinity for oxygen, and all of them may be made to combine with it. In like manner the metals have strong affinities for, and may easily be made to combine with chlorine, bromine, iodine, fluorine (to which may be added cyanogen), as well as sulphur, selenium; and in many cases, phosphorus and carbon; in a few, hydrogen and silicon. Metals also combine with each other. Owing to the extensive range of these affinities, metals are rarely found uncombined, or native, as it is called, and the operations of metallurgy are chiefly such as are required to separate metals from the compounds in which they occur, which are called their *ores*. Oxygen, in the atmosphere and in water, being far more abundant than the other metalloids, metals are chiefly found oxidised, and are therefore commonly extracted from the ores by processes of deoxidation, or reduction, as it is termed.

METALS WITH OXYGEN.

Metals differ in the degree of their attraction for oxygen. Some metals, such as potassium, rapidly combine with oxygen when exposed to the air, or when brought in contact with water or with any other oxidised compound. Others, such as iron, are very slowly oxidised by exposure to the air at ordinary temperatures, and hardly act on cold water; but at a strong red-heat they burn in the air, and decompose the vapour of water, setting free hydrogen gas. Others again combine with oxygen when heated in air, but do not decompose water at all, such as copper. These, as well as the preceding, are in general easily oxidised by acids; and their attraction for oxygen is such that their oxides, once formed, are not decomposed by a red-heat alone, without the help of combustible matter. Finally, some metals, such as gold and silver, &c., have much less attraction for oxygen. They are not so easily or directly oxidised, and the oxides, once formed, are quite easily decomposed by a red-heat, being resolved into metal and oxygen.

When metals combine with oxygen, they form three classes of oxides.

1st. Bases, or basic oxides, the most usual formula of which is MO; such oxides are called protoxides. Besides protoxides, a pretty numerous class of basic oxides has the formula M_2O_3: these are sesquioxides. A very few basic oxides have the formula MO_2: these are binoxides or deutoxides. Potash, KO, is an example of a protoxide; sesquioxide of iron, Fe_2O_3, of a sesquioxide, and deutoxide of tin, SnO_2, of a basic deutoxide.

All basic oxides form neutral salts by combining with acids. In all such cases there is produced, besides the neutral salt, a quantity of water, the oxygen of which, according to the most probable view, is derived from the metallic oxide. Its hydrogen must therefore be derived from the acid, and in the case of the hydrogen acids with simple radical, this is admitted by all. For example, when potash, KO, acts on hydrochloric acid, HCl, the change is universally admitted to be as follows:—

$$KO + HCl = HO + KCl.$$

That is, the basic oxide, and the hydrogen acid, give rise to water and to chloride of potassium, both neutral substances. Neither have we any difficulty in adopting the same view in the case of a hydrogen acid with a compound radical; for example, hydrocyanic acid:—

$$KO + HCy = HO + KCy: \text{ or, } KO + H, C_2N = HO + K, C_2N.$$

But when we bring potash in contact with oil of vitriol or strong sulphuric acid, most chemists are inclined to adopt a different explanation of phenomena precisely analogous. They call the acid hydrated sulphuric acid, HO, SO_3, and express the action as follows:—

$$KO + HO, SO_3 = HO + KO, SO_3.$$

Here, it will be observed, the results are quite similar to those in the preceding cases; namely, the separation of water, and of a neutral salt, in this case sulphate of potash. And yet we adopt a different explanation, at least on the older view of acids and salts, supposing the water to pre-exist in the acid, and to be replaced by the oxide. As it is, however, quite unphilosophical to employ two explanations of analogous facts if one will suffice, we are thus induced to prefer the newer view of acids and salts formerly alluded to, which admits of our giving the same explanation of the two cases. According to this view, then, we consider oil of vitriol a hydrogen acid, H, SO_4, and express the change thus :—

$$KO + H, SO_4 = HO + K, SO_4.$$

On comparing this with the equation above given for the action of potash on hydrocyanic acid in its second form, it will be seen that the analogy is perfect. Both acids and both salts contain a compound acid radical, in the one case C_2N, in the other SO_4 ; and both differ from the acid and salt of chlorine in the fact of their radicals being compound, or rather *known to be* compound : for chlorine may very possibly be itself a compound radical, although at present we must view it as simple, because it is undecomposed.

The action of a basic sesquioxide, and of a basic deutoxide, on an acid, say sulphuric, is represented as follows on both the different theories of acids :—

$$M_2O_3 + 3(HO, SO_3) = 3HO + M_2O_3, 3SO_3 :$$

or,

$$M_2O_3 + 3(H, SO_4) = 3HO + M_2, 3SO_4.$$

$$MO_2 + 2(HO, SO_3) = 2HO + MO_2, 2SO_3 :$$

or,

$$MO_2 + 2(H, SO_4) = 2HO + M, 2SO_4.$$

Here we see that, for every equivalent of oxygen in the base, an equivalent of acid is required to form a neutral salt ; and that, on the new view, the resulting neutral salts are compounds corresponding to the basic oxides from which they are formed. Thus we have—

Basic Oxide.	Corresponding Neutral Salt.		
$M + O$ . .	$M + SO_4$,	or in general terms,	$M + R$
$M_2 + O_3$.	$M_2 + 3SO_4$	,, ,,	$M_2 + R_3$
$M + O_2$.	$M + 2SO_4$	,, ,,	$M + R_2$

Such are the most important chemical relations of the basic oxides, which include, among the protoxides, the strongest alkalies and alkaline earths.

2nd. Neutral or indifferent metallic oxides. These appear, by combining with an additional quantity of oxygen, to have lost the basic, without acquiring the acid character. They commonly enter into few combinations of any kind. Their composition varies, being sometimes M_3O_4, and sometimes MO_2. Red oxide of lead, Pb_3O_4, is an example of the former ; hyperoxide of manganese, MnO_2, of the latter.

When heated with acids, oxygen is given off, while a basic oxide is formed, and acts on the acid as above, forming a neutral salt. Thus, peroxide of manganese, heated with oil of vitriol, gives—

$$Mn\,O_2 + HO, SO_3 = Mn\,O, SO_3 + HO + O:$$

or,

$$Mn\,O_2 + H, SO_4 = Mn, SO_4 + HO + O.$$

3rd. Metallic acids. These are pretty numerous. When the same metal forms a basic oxide and an acid, the latter always contains more oxygen. There are several different formulæ among metallic acids. They are sometimes sesquioxides, as $As_2\,O_3$, arsenious acid; sometimes deutoxides, as titanic acid, $Ti\,O_2$; very often teroxides, as chromic acid, $Cr\,O_3$; occasionally $\frac{2}{5}$ oxides, as arsenic acid, $As_2\,O_5$; and in one case a quadroxide, as osmic acid, $Os\,O_4$.

Metallic acids, when heated, generally lose oxygen, and are reduced to the basic oxide; this takes place especially if they are heated with acids. Thus manganic acid, $Mn\,O_3$, heated with sulphuric acid, yields oxygen gas and neutral sulphate of the protoxide.

$$Mn\,O_3 + HO, SO_3 = Mn\,O, SO_3 + HO + O_2:$$

or,

$$Mn\,O_3 + H, SO_4 = Mn, SO_4 + HO + O_2.$$

When we wish to form metallic acids, we commonly heat or deflagrate the metal, or its lower oxides, along with an alkaline nitrate or chlorate, in which case the acid that is formed remains in combination with the alkali. Or chlorine gas is passed through water in which the oxide, in fine powder, is suspended sometimes along with an alkali, sometimes alone.

When our object is to deprive metals of the oxygen with which they are combined, or to reduce them, as it is called, to the metallic state, different methods are followed, according to the attraction of the metal for oxygen.

1. The oxides of the noble metals, such as mercury, silver, gold, platinum, &c. are reduced by a red-heat alone.

2. The oxides of a large number of metals, such as copper, iron, tin, barium, or potassium, can only be reduced by the united action of heat and combustible matter, such as carbon, hydrogen, &c. The change is as follows: $M\,O + C = M + C\,O$; or $M\,O + H = M + H\,O$. In the former case carbonic oxide gas, in the latter water, is produced, and being expelled by the heat, leaves the metal pure. The use of carbon for reduction is the foundation of all the metallurgic processes on the large scale.

As the ores, however, are not pure, substances called fluxes are added to cause the impurities to melt, forming a fluid glass, below which the melted metal is found.

Perhaps the most powerful reducing or deoxidising compounds at a red-heat are the formiates, and cyanide of potassium. The formula of a formiate is $MO, C_2HO_3 = MO + HO, 2CO$: so that it yields at a red-heat carbonic oxide gas, a body having much attraction for oxygen. Cyanide of potassium is $KCy = K, C_2N$; and, as Liebig has pointed out, it combines the very powerful deoxidising agency of carbon and of potassium. Its reducing power is very great.

3. The oxides of the metals of some of the alkalies and earths, whose attraction for oxygen is very strong, and which are with difficulty reduced in any other way, are decomposed by a powerful galvanic battery so as to yield the metals. This is only done on a very small scale.

4. Many oxides in solution are reduced to the metallic state by other metals having a stronger attraction for oxygen, which take the place of the metal previously in solution. Thus copper precipitates silver, and iron precipitates copper.

5. Many oxides in solution, that is, combined with acids, are reduced to the metallic state by what are called deoxidising agents. Thus the noble metals, such as gold, platinum, &c., are reduced by sulphurous, phosphorous, and hypophosphorous acids and their salts; by oxalic and formic acids and their salts: gold is even reduced by hydrogen gas and by solutions of protosalts of iron, such as green vitriol. In all these cases the reducing or deoxidising agent is oxidised; phosphorous acid, for example, yielding phosphoric, and protoxide of iron passing into peroxide, at the expense of the metallic oxide.

The electrotype, in which copper, silver, gold, or platinum are reduced to the metallic state in such a way as to form coherent masses similar to the hammered metals, and by which the most beautiful and perfect copies of medals may be taken, is a process depending partly on the reducing agency of the galvanic battery, partly on that of hydrogen gas, which, instead of escaping uncombined at the negative pole, is then oxidised at the expense of the metallic oxide. In this process, which is minutely described in works devoted to the subject, it is essential that the electric current should be slow and uniform, otherwise the metal is deposited in different states. Plating and gilding by this process have a beautiful appearance, and are perfectly adapted for objects not subjected to much wear or friction.

METALS WITH HYDROGEN.

Only a few metals unite with hydrogen, and these form gaseous and combustible compounds not yet known in a pure state, but only in a state of mixture with hydrogen gas. The following metals only are as yet known to combine with hydrogen :—zinc, potassium, arsenic, antimony, and tellurium.

METALS WITH NITROGEN.

Until lately metals were not known to combine with this element; but we are now acquainted with compounds of nitrogen with copper, chromium, and mercury. These compounds are black or dark-brown powders, which may be obtained by passing dry ammoniacal gas over the oxides of the metals, gently heated, water being at the same time produced and nitrogen gas liberated. Thus, when oxide of copper is acted on by ammonia, we have $6\,Cu\,O + 2\,N\,H_3 = 6\,H\,O + N\,Cu_6 + N$. Like the compounds of nitrogen with chlorine and iodine, these compounds are easily made to explode, their elements separating with violence, and with a flash of light, by a gentle heat or friction, or percussion. It is possible, or indeed probable, that fulminating gold and silver, prepared by the action of ammonia on the oxides of these metals, and the explosive tendencies of which render them so very dangerous, are in reality the compounds of the metals with nitrogen. These must be distinguished from the other fulminating silver which, like fulminating mercury, is a compound of oxide of the metal with fulminic acid.

METALS AND CHLORINE.

The attraction or affinity between chlorine and metals is very strong. Many metals, such as potassium, copper, gold, antimony, &c., combine instantaneously with chlorine without the aid of heat, but with the phenomena of combustion. Others, such as mercury, &c., burn in chlorine only when they are heated in the gas. By combining with chlorine, metals give rise to chlorides, which may often be more advantageously formed by other means than by direct combination with the gas. Other methods of obtaining chlorides are the following :—

1. Chlorine gas is passed over the oxide or sulphuret of the metal heated to redness. In many cases the affinity of chlorine prevails, and the oxygen or sulphur is expelled. $M\,O + Cl = M\,Cl + O$.

2. Hydrochloric acid gas is passed over the oxide or the

sulphuret heated to low redness. Here the affinity of hydrogen for oxygen or sulphur, added to that of chlorine for the metal, effects decomposition which chlorine alone could not accomplish. $MO + HCl = MCl + HO$: $MS + HCl = MCl + HS$.

3. To the solution of an oxide, in water or in acids, hydrochloric acid or a soluble chloride are added. If the metal forms an insoluble chloride, that is at once precipitated, showing that the change must be, as in the case of the dry gas, $MO + HCl = MCl + HO$. If the metal, as in the case of potassium, forms a soluble chloride, then the addition of hydrochloric acid causes no visible change; but on evaporation, crystals are deposited, which are generally found to be of a chloride, and free from oxygen or hydrogen. Thus, potash, KO, with hydrochloric acid, HCl, undergoes, in solution, no change of appearance at first; but on evaporation yields cubical crystals, which are found to be KCl.

4. Some metals, as gold and platinum, are converted into chlorides by dissolving them in aqua regia, or nitro-muriatic acid, and evaporating gently to dryness with an excess of hydrochloric acid. The dry residue is pure chloride.

When metals are combined with chlorine they may be reduced to the metallic state by various means.

1. Some chlorides are reduced by heat alone, which expels the chlorine. This is the case with almost all the chlorides of the noble metals.

2. Other chlorides are reduced by the action of another metal. Thus, chloride of platinum or chloride of silver is reduced by means of zinc.

3. Many chlorides are reduced by hydrogen gas at a red-heat, but not by charcoal, as oxides are.

4. The chlorides of the noble metals are reduced by boiling their solutions with a formiate; those of gold and platinum also by the protosulphate of iron. Chlorides may also be reduced by fusion with formiates or with cyanide of potassium.

What has been said of the relation of metals to chlorine applies almost exactly to their relations with bromine, iodine, fluorine, and cyanogen, which in its combination with metals plays the part of a salt radical, entirely analogous to chlorine.

The chlorides, bromides, iodides, and cyanides of metals are true salts, for the most part neutral salts. Indeed, sea salt, the type of all salts, is chloride of sodium, $NaCl$. None of these compounds possess decided acid or basic characters; but the chlorides, &c., are capable of combining together and forming double chlorides, &c., which have been compared by Bonsdorff to oxygen salts. Thus viewing, as he did, chromate of potash,

KO, CrO_3, as an oxygen salt, he viewed the following compound, $KCl, HgCl_2$, as a chlorine salt. The former contains, according to him, an oxygen acid, CrO_3, and an oxygen base, KO; the latter, a chlorine acid (bichloride of mercury), $HgCl_2$, and a chlorine base, KCl, (chloride of potassium). But it is to be observed that neither KCl nor $HgCl_2$ have basic or acid properties; they are, on the contrary, neutral salts, and, according to the more probable views now beginning to prevail as to the true nature of salts, which are considered compounds of metals with salt radicals, the compound $KCl + HgCl_2$ is viewed as a double salt. The same view applies to a large number of analogous double chlorides, bromides, iodides, fluorides, and cyanides.

METALS WITH SULPHUR.

All the metals are capable of combining with sulphur, and many metallic sulphurets are found native: those of iron, copper, lead, antimony, zinc, and bismuth in abundance: those of mercury, silver, cadmium, and some others, more sparingly.

Most metals when heated along with sulphur combine with it; but in many cases sulphurets are obtained by the action of sulphur compounds on the oxides, or by the deoxidation of sulphates.

1. When an oxide is exposed to the action of sulphuretted hydrogen gas, aided by heat, water and a sulphuret are formed, $MO + HS = HO + MS$. The same change takes place when a solution of sulphuretted hydrogen or a current of the gas is made to act on solutions of oxides in acids. The sulphurets of the following metals may be thus obtained, being all insoluble in water:—

Group I. Metals, the oxides of which, in acid solutions, are precipitated as sulphurets by sulphuretted hydrogen.

Metals.	Colour of Precipitate.	Metals.	Colour of Precipitate.
Cadmium	Orange.	Platinum	Black.
Lead	Black.	Iridium	Black.
Bismuth	Black.	Gold	Black.
Copper	Black.	Tin, protoxide	Brown.
Silver	Black.	Tin, peroxide	Yellow.
Mercury	Black.	Antimony	Reddish orange.
Palladium	Black.	Molybdenum	Brown or red.
Rhodium	Black.	Tungsten	Brown.
Osmium	Black.	Vanadium	Dark brown.
Tellurium	Yellow.	Arsenic	Orange yellow.

The other metals are not precipitated by sulphuretted hydrogen, but the following yield sulphurets when their oxides in solution are acted on by hydrosulphuret of ammonia (sulphuret of ammonium), or by a soluble metallic sulphuret :—

Group II. Metals, the oxides of which are precipitated as sulphurets by soluble sulphurets, although not by sulphuretted hydrogen.

Metals.	Colour of Precipitate.	Metals.	Colour of Precipitate.
Iron	Black.	Cobalt	Black
Manganese	Flesh colour.	Nickel	Black*
Zinc	White.		

The remaining metals, those of the alkalies and earths, form a third group, the sulphurets of which being soluble do not appear as precipitates.

2. When a sulphate of a metallic oxide, MO, SO_3, or M, SO_4, is acted on by hydrogen or carbon at a strong red-heat, it is entirely deoxidised, and the sulphuret of the metal is left. Thus, if sulphate of baryta, KO, SO_3, or K, SO_4, be mixed with about one-sixth of its weight of charcoal, and exposed for two hours to a bright red-heat in a vessel closed, except where a small aperture is left for the escape of gaseous matter, carbonic oxide is given off and sulphuret of barium is left ; $Ba\,O, SO_3 + C_4 = 4\,CO + Ba\,S$.

The sulphurets of each metal are commonly equal in number and analogous in composition to its oxides. Metallic sulphurets unite together, as oxides do, and produce double sulphurets or sulphur salts, which are closely analogous to oxygen salts.

Thus we have—

	Oxygen Salts.		Sulphur Salts.	
	Oxygen Acids.	Oxygen Base.	Sulphur Acids.	Sulphur Base.
With Molybdenum	$Mo\ O_3$ +	$K\,O$	$Mo\ S_3$ +	$K\,S$
With Arsenic	$As_2\ O_3$ +	$K\,O$	$As_2\ S_3$ +	$K\,S$
———	$As_2\ O_5$ +	$3K\,O$	$As_2\ S_5$ +	$3K\,S$.

Of course, if we view the oxygen salt, $As_2\ O_5$,.3 KO, for example, as a compound of a metal with a salt-radical, $As_2\ O_8, K_3$, the corresponding sulphur salt, $As_2\ S_5$, 3 KS, becomes $As_2\ S_8, K_3$. The analogy between the compounds of sulphur with metals, and those of oxygen with the same bodies, has been shown by Berzelius to be very complete.

With selenium and tellurium metals form compounds very analogous to the sulphurets.

With phosphorus some metals combine and yield compounds called phosphurets, few of which are known. The alkaline phosphurets, as those of barium and calcium, yield by the action of water phosphuretted hydrogen gas, which takes fire spontaneously.

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* Alumina is precipitated white by soluble sulphurets, but the precipitate is not sulphuret of the metal, but only hydrated oxide.

Metals combine in several cases with carbon, forming compounds which are called carburets. They are generally brittle solids, and the only useful carburets are those of iron, which are two valuable compounds, steel and cast iron.

As all the compounds of metals with chlorine, bromine, iodine, fluorine, sulphur, and selenium, contain along with the metal a radical which forms an acid by combining with hydrogen, while the metal generally forms a base with oxygen, the question arises what takes place when such metallic compounds are dissolved in water? Does the metal seize the oxygen, and the radical the hydrogen of an equivalent of water, and do the acid and base thus produced combine together?

In the case of an insoluble chloride, such as that of silver, we know that the hydrochloric acid does not combine with the oxide when both are mixed in solution, for the precipitate is found to be $Ag\,Cl$. Here the oxygen of the base and the hydrogen of the acid must have formed water: $Ag\,O + H\,Cl = HO + Ag\,Cl$.

But when hydrochloric acid, $H\,Cl$, is mixed with potash, $K\,O$, or, what comes to the same thing, when chloride of potassium, $K\,Cl$, is dissolved in water, what is the compound present in the liquid? Is it $K\,Cl$ simply dissolved as such? or, is it a salt, $K\,O + H\,Cl$? We know that the liquid, if evaporated, yields crystals of $K\,Cl$, but it is possible that this compound may be formed by the force of cohesion when it crystallises, and may not be previously present.

The general opinion of chemists is that in most cases soluble chlorides, sulphurets, &c., dissolve as such in water; but that in some cases the hydrogen acid does appear to combine with the oxide.

If $K\,Cl$, in dissolving, decomposes water, and forms $K\,O + H\,Cl$, then we must admit that in the act of crystallising, when $K\,Cl$ separates, water is again recomposed. These continual decompositions and recompositions of water, without any visible change of properties, are so improbable that in most cases we cannot admit their occurrence.

But there are cases in which the solution of a chloride, &c., is attended with a change of properties. Thus, chloride of magnesium and chloride of aluminum when dissolved in water, cannot again be obtained in the anhydrous form. On evaporation oxide of magnesium or of aluminum are left, while hydrochloric acid escapes. Again, dry sesquichloride of chromium is peach-coloured, but its solution is deep green, the colour of all solutions containing sesquioxide of chromium; dry chloride of cobalt is blue, and its solution is pink, like all solutions containing oxide of cobalt.

In these and a few more similar cases, we can hardly doubt that water is decomposed when a chloride, &c., is dissolved; but in the great majority of cases we have no evidence of this; and, therefore, it may be laid down as a general rule that chlorides and analogous compounds dissolve as such in water, and that hydrogen acids mutually decompose metallic oxides, yielding water and compounds of the metal with the radical of the hydrogen acid. To this rule there are some exceptions; some chlorides, &c., in dissolving, decompose water, producing a hydrogen acid and an oxide; and hydrogen acids are capable of combining with some oxides without mutual decomposition, the compounds, however, not being very stable.

METALS WITH METALS.

Metals are capable of combining together, and forming compounds which retain the metallic character, and many of which are highly useful. They are called alloys, except where mercury is one of the metals, when they receive the name of amalgams. Thus, brass is an alloy of copper and zinc; pewter an alloy of lead and tin; German silver an alloy of copper, zinc, and nickel. The metal used for silvering the backs of mirrors is an amalgam of tin and lead; that is, it contains mercury with these metals. The alloys will be briefly described hereafter.

The progress of modern chemistry has added largely to the number of the elementary metals. Before the middle of last century the metals known were only such as had long been used in the arts or in medicine, and did not exceed twelve in number. From that period many new metals were gradually discovered in the mineral kingdom; and, in 1807, Davy's discovery of the metals of the alkalies at once added a numerous class of metals to the list. Wollaston and Smithson Tennant had previously, in 1803, discovered the four remarkable metals associated with platinum in its ores. The whole number of ascertained metals is now forty-two; and within the last year or two, Mosander has announced the discovery of three new metals, accompanying cerium and yttrium, Rose that of two, associated with columbium, and Klaus that of one more in the ore of platinum. These, if established, will raise the number to forty-eight.

In considering the metals individually, we shall arrange them in groups or classes, according to their affinities for oxygen and to their chemical relations.

CLASS I. includes twelve metals, subdivided into three well-marked orders.

Order 1. Metals of the alkalies proper, namely—

Potassium. Sodium. Lithium.

These metals have so strong an affinity for oxygen that they are rapidly oxidised by exposure to the air, and decompose water with violence, disengaging hydrogen gas, which generally takes fire. Their oxides are powerful bases or alkalies, very soluble in water and very caustic.

Order 2. Metals of the alkaline earths, namely—

Barium. Strontium. Calcium. Magnesium.

These metals have also a very strong affinity for oxygen, and, except magnesium, they decompose water at ordinary temperatures, but without flame. Their oxides are powerful bases, but less soluble and caustic than the alkalies; indeed, oxide of magnesium is insoluble. As they are thus intermediate between the alkalies and the earths proper, they are called alkaline earths.

Order 3. Metals of the earths proper, namely—

Aluminum. Glucinum. Yttrium.
Thorium. Zirconium.

These metals do not decompose water at ordinary temperatures, but burn in air when heated, forming oxides, which are less powerful bases than the preceding; and being quite insoluble in water and earthy in aspect, they are called the earths.

CLASS II. includes 30 metals; which are also subdivided into three orders. All these metals combine with oxygen, and in general their protoxides are insoluble and of an earthy aspect, but coloured, and have basic characters, in many cases very powerful. A considerable number of these metals form acids with a larger proportion of oxygen. This class contains all the heavy metals, and all those which, from their malleability, ductility, &c., have long been used by mankind.

Order 1. Metals, the protoxides of which are powerful bases, but which do not decompose water unless with the aid of a red-heat; namely—

Manganese. Tin. Cobalt.
Zinc. Cadmium. Nickel.
Iron.

Order 2. Metals which do not decompose water at any temperature; but the oxides of which, once formed, cannot be reduced by heat alone: namely—

Arsenic
Chromium.
Vanadium.
Molybdenum.
Tungsten.
Columbium.
Antimony.
Uranium.
Cerium ?
Lantanium ?
Bismuth.
Titanium.
Tellurium.
Copper.
Lead.

It is doubtful whether cerium and lantanium do not belong to the preceding order, to which also belong, in all probability, the three new metals of Mosander, didymium, erbium, and terbium.

Order 3. Metals, the affinity of which for oxygen is so feeble that their oxides are reduced by a red-heat: namely,

Mercury.
Silver.
Gold.
Platinum.
Palladium.
Rhodium.
Osmium.
Iridium.
Ruthenium ?

Owing to the comparatively feeble affinity for oxygen of these metals, they have no tendency to rust when exposed to the air, as iron does, for example, from its strong attraction for oxygen. Hence they retain the brilliant lustre of their polished surface, and do not wear by exposure to the air. They are therefore often called the noble or precious metals.

We now proceed to the description of the separate metals, which may be made very brief in consequence of our having so minutely described the general chemical characters of metallic bodies, the analogy among which is so great that the description of one is applicable, with but little change, to the others.

METALS.—CLASS I.

Order 1.—Metals of the Alkalies Proper.

14. Potassium. $K = 39{\cdot}15$.

Syn. *Kalium.*—This metal occurs chiefly in the ashes of land plants as oxide or potash united to carbonic acid; it is also found as chloride in the ashes of sea plants. Many abundant rocks, such as felspar (with all its derivatives, such as clays), and mica, besides many simple minerals, contain potash in considerable quantity. It is contained also in most fertile soils, being necessary to the growth of plants, in the form of potash. Potassium was discovered in 1807, by Davy, who obtained it by the action of a powerful galvanic battery on hydrate of potash, KO, HO. At the negative pole oxygen was given off, and at the positive pole appeared hydrogen, derived from the water of the hydrate, along with the globules of a metal resembling mercury, which took fire in the air and burnt, reproducing potash. This expensive and troublesome method has long been abandoned, and potassium is now prepared by the action of charcoal at a white heat on carbonate of potash, KO, CO_2.

A mixture of carbonate of potash with finely divided charcoal is first prepared by igniting cream of tartar in a covered crucible, which leaves such a mixture, well known as the black flux. This, while still warm, is mixed with a considerable proportion of charcoal in coarse powder and small fragments recently ignited and allowed to cool in a covered crucible. The whole is now introduced into one of the hammered iron bottles used for holding mercury, coated outside with a mixture of sand and clay. The bottle is placed horizontally in a wind furnace, and a short wide tube of iron is fitted to it, to which tube is attached a copper receiver, partly filled with good naphtha, and having a diaphragm of copper, and on the further side of the receiver an aperture for the escape of gas, opposite the tube of the bottle; so that, if necessary, a strong steel rod may be introduced through this aperture and another in the upper part of the diaphragm into the tube, for the purpose of cleaning it out, as it is apt to become choked. The receiver with the naphtha being surrounded with ice, a steady and uniform strong red or white-heat (by means of dry wood, the flame of which plays all round the bottle,) is applied to the bottle, and after a time potassium, which is known by the appearance of its pink flame at the mouth of the tube, distils over, accompanied with carbonic oxide gas, and with a grey powder, which is the cause of the occasional choking of the tube. The potassium drops into the naphtha, which protects it from the action of the air. To purify it entirely, it is redistilled in a small iron retort along with a little naphtha into a receiver containing that liquid.

In this process the carbon deprives the oxide of potassium and the carbonic acid of their oxygen, forming carbonic oxide gas. $KO, CO_2 + C_2 = K + 3\ CO$. Were this all, we should have no other product but potassium and carbonic oxide. Unfortunately, however, carbonic oxide at a red-heat, enters into combination with potassium, forming the grey powder above mentioned; the composition of which is $7\ CO + K_3 = C_7O_7, K_3$. If, therefore, we consider the products obtained from 4 eq. of carbonate of potash, they ought to be as follows, if the grey compound were not formed, $4\ (KO,CO_2)+C_8=K_4+12\ CO$. Instead of obtaining 4 eq. of potassium, however, from 4 eq. of carbonate, we only obtain 1 eq. as metal, the remaining 3 eq. combining with carbonic oxide to form the grey powder. $K_4+12\ CO=(C_7\ O_7,\ K_3)+5\ CO+K$. This is the reason why the above process is not nearly so productive as might be expected. The grey powder must be kept under naphtha, as it is liable to be altered if exposed to the air, and especially to take fire and explode, if moistened with water. (This compound, by the slow action of the air, is converted into a very remarkable salt, rhodizonate of potash, to be hereafter mentioned, when carbonic oxide is treated of as a compound radical.)

Potassium is a metal of a bluish-white colour, and a high degree of metallic lustre, so that a melted portion of it, under naphtha, resembles mercury or melted silver. At ordinary temperatures, it is so soft as to yield easily to the finger. At 150° it is quite fluid, and if cooled to 32°, it becomes brittle. At a low red-heat it boils, and may be distilled unchanged. Its Sp. G. is 0·865, so that it floats on the surface of water.

When exposed to the air it is instantly tarnished by the formation of a film of oxide; and after a short time the whole is oxidised and converted into a white solid oxide, which soon attracts water from the atmosphere. Potassium must therefore be kept under naphtha, a liquid containing no oxygen. When heated in the air, potassium takes fire, and burns with a beautiful pink flame, oxide being formed. So powerful is its affinity for oxygen, that when thrown on the surface of water, it instantly decomposes it, with so much disengagement of heat as to set fire to the hydrogen gas which is separated. $K+HO=KO+H$. The hydrogen burning causes the potassium also to burn, combining with the oxygen of the air, and the globule swims about until it is consumed, burning on the surface of the water with a beautiful pink flame. The same phenomenon appears if the metal be placed in a small hollow on the surface of a piece of ice, when it instantly bursts into flame.

The affinity of potassium for oxygen and the other metalloids is so powerful that it has been the means of isolating many metals and some metalloids, whose attraction for oxygen, &c., is too strong to be overcome by the usual means. Thus potassium decomposes the oxides or chlorides of aluminum, glucinum, yttrium, thorium, and zirconium, and the boracic and silicic acids. It is, consequently, a very powerful instrument of research.

The compounds of potassium to be here described are those which it forms with the metalloids.

POTASSIUM AND OXYGEN.

Potassium forms two compounds with oxygen, a protoxide KO, and a peroxide KO_3.

a. Protoxide of Potassium. $KO = 47{\cdot}163$.

This oxide is only formed when potassium is oxidised in dry air, or oxygen. It is a white powder, which rapidly absorbs moisture from the air, and deliquesces. It is now converted into the usual form, namely, hydrated oxide of potassium, or hydrate of potash.

SYN. *Caustic Potash.* $KO, HO = 56{\cdot}176$.—This important compound is best prepared by acting on pure carbonate of potash, dissolved in water, so as to deprive it of carbonic acid. Two parts of carbonate are dissolved in twenty of boiling water in an iron pot, and one part of quick lime, being previously slaked by covering it with boiling water, so as to form a kind of cream of slaked lime, is added to the boiling liquid in small portions, the mixture being allowed to boil a minute or two after each addition. When all the lime has been added, the whole is to be boiled for five minutes, care being taken to keep up the original quantity of water; since, with less water, the potash actually takes back the carbonic acid from the lime. The vessel, which ought to be more deep than wide, is then covered up with its lid, and allowed to stand for 24 hours. At the end of that time, if the above directions have been exactly followed, $\frac{19}{20}$ of the liquid may be decanted off perfectly clear and colourless. This is a pure solution of potash, and to obtain the hydrate, we have merely to boil it rapidly down, in a clean deep iron or silver vessel, till the residue flows like oil. It is then poured out on a plate of silver, and, on cooling, broken up into fragments, and preserved in well-stopped bottles.

In the above process, the lime deprives the carbonate of potash of its carbonic acid, forming insoluble carbonate of lime. $KO, CO_2 + CaO, HO = CaO, CO_2 + KO, HO$. By slaking the lime with hot water, it falls to so fine a powder that every particle acts, and we are thus enabled to use very little more than the atomic proportion of quick-lime, which would be about 28 to 69, instead of 1 to 2, or 28 to 56, as we employ. Again, by adding the lime gradually, and constantly boiling, the carbonate of lime assumes a very dense form, and settles perfectly to the bottom ; whereas, if the lime were all added at once, it would yield a very bulky carbonate, from which the solution of potash would be with difficulty separated. By allowing the liquid to clear in the covered vessel, we avoid filtration and, consequently, the bringing the potash in contact with the air, from which it absorbs carbonic acid, and is re-converted into carbonate. So effectual is the above process, that the decanted liquid does not effervesce with acids, if carefully prepared ; and if it be rapidly boiled to dryness, the solid hydrate may be also obtained free from carbonic acid.

The hydrate of potash is so valuable a re-agent to the chemist, that I have described minutely the best method of preparing it, which, as generally happens, is also the most simple. The solution, or aqua potassæ, is daily used in the ultimate analysis of organic bodies, to absorb carbonic acid ; and for this purpose, as well as for many others, it is obtained sufficiently pure from the pearlash, or impure carbonate of potash of commerce. The pearlash is to be treated precisely as the pure carbonate in the above process ; and the decanted solution of caustic potash is to be boiled down until crystals begin to form in the boiling liquid, which is then allowed to cool in well-stopped bottles of green glass. The crystals are sulphate of potash, a salt present in the pearlash, which is insoluble in a strong solution of caustic potash. On cooling, therefore, the whole of the sulphate crystallises out, so that not a trace is left in the liquid. The clear liquid, decanted from the crystals, now contains no impurity, except chloride of potassium, which, for most purposes, is of no importance. It has a Sp. G. of 1·25 to 1·35, and is ready for use in organic analysis. If boiled to dryness, it yields a hydrate of potash, far purer than the hydrate of commerce, inasmuch as it is free from sulphate.

Hydrate of potash cast into small sticks, is much used by surgeons as a powerful caustic. The chief objection to its use is that, owing to its attraction for water, it deliquesces, and spreads farther than is intended. But in careful hands, it is easily managed, and is often used in preference to the knife, for opening glandular swellings, such as buboes, which have suppurated. When thus opened, and when the caustic has been applied to the inner surface of the cavity, they appear to heal better than when opened with the lancet. In chemistry hydrate of potash is much used for the decomposition of minerals, by fusion with them, and for drying certain gases.

The solution of potash, aqua potassæ, or liquor potassæ, has the acrid corrosive taste of the hydrate; and when rubbed between the fingers, gives them a soapy feel, forming, in fact, soap with the oil of the skin. It turns infusion of red cabbage, of violets, dahlias, &c., green, and restores the blue of litmus reddened by acids. It is powerfully alkaline, or basic, neutralising all acids. Its great attraction for carbonic acid has been already mentioned as the reason of its being used in organic analysis, for the purpose of absorbing the carbonic acid derived from the carbon of the substance, and enabling us to ascertain its weight. For the same reason, potash in the form of solid hydrate, or in solution, must always be protected from the carbonic acid of the atmosphere. The solution, when of Sp.G. 1·060, is used in medicine as an antacid and lithontriptic. The chief use of potash is unquestionably that of promoting the growth of plants, to which it is generally essential, although it may frequently be replaced by soda or lime. Its function appears to be that of fixing the carbonic acid of the atmosphere, which, with the elements of water, gives rise to the chief vegetable products, as will be explained in the second part. Hence, all fertile soils contain it; hence also the value of the ashes of vegetables, as manure, depends, in a great measure, on the potash they contain; and the same remark applies to animal manures. Cow-dung, for example, is very rich in potash.

The presence of potash in any solution is best ascertained by the action of bichloride of platinum in solution, which, if any notable quantity of potash be present, forms with it a pale yellow precipitate of the double chloride of platinum and potassium. If the proportion of potash be very small, no precipitate may appear; in this case, the liquid to be tested may be first concentrated by evaporation, and then again tested with the platinum salt, when the precipitate will in all probability appear; or alcohol may be added to the first mixture, in which the double chloride is quite insoluble. The only uncertainty in this test is, that ammonia gives a similar precipitate; so that we must first ascertain if ammonia be present; and if so, expel it by a red-heat, before testing for potassium.

Perchloric acid also causes in solutions containing potash, a white precipitate of perchlorate of potash, sparingly soluble in water, and quite insoluble in alcohol, so that if but little potash be present, alcohol ought here also to be added.

An excess of tartaric acid produces, after a time, a crystalline deposit of cream of tartar, in solutions containing potash, more especially if well stirred with a glass rod, which causes the deposit to appear in streaks on the glass.

An alcoholic solution of carbazotic acid causes a yellow crystalline precipitate in solution of potash.

Lastly, hydrofluosilicic acid causes a gelatinous semi-transparent precipitate of silicofluoride of potassium, when added to solutions of potash: of all these tests, the most certain is the bichloride of platinum, with the aid of alcohol.

b. Peroxide of Potassium. $KO_3 = 63{\cdot}176$.

This oxide is formed by passing oxygen over red-hot potash. It is an orange-yellow powder, which, when thrown into water, is decomposed, oxygen being given off, and potash being found in the liquid.

POTASSIUM WITH HYDROGEN AND NITROGEN.

With hydrogen, potassium forms two compounds, one of which appears to be a solid, the other a gas. The latter seems to take fire spontaneously in contact with air, and is probably formed when potassium acts on water. The former is produced when potassium is heated in hydrogen gas. It is a grey solid decomposed by water.

When potassium is heated in dry ammonia, an olive-coloured solid is formed, which is composed of potassium and amide (amidogen), K, NH_2. When this is heated, ammonia is given off, and there is left a substance resembling graphite, which is a compound of potassium and nitrogen, $3\,(K, NH_2) = 2\,NH_3 + NK_3$. This compound has been little examined.

POTASSIUM WITH CHLORINE, BROMINE, IODINE, AND FLUORINE.

With all these elements potassium combines, with each in one proportion only, forming compounds which are very analogous to each other.

Chloride of Potassium. $KCl = 74{\cdot}57$.

This compound is a neutral salt, very similar to sea-salt. It is found in considerable quantity in the ashes of plants, especially of sea-plants. It is formed when potash is neutralised by hydrochloric acid, and the solution evaporated so as to form crystals. $KO + HCl = HO + KCl$. It is also left when chlorate or perchlorate of potash is heated so as to expel all the oxygen $KO, ClO_5 = KCl + O_6$.

It has a saline and bitterish taste, and is not much more soluble in hot than in cold water. It crystallises, like sea-salt, in cubes. It is only used, when very cheap, in the manufacture of alum. It cannot be substituted for sea-salt, as a condiment, or antiseptic.

Iodide of Potassium. $KI = 165{\cdot}45$.

This salt, which is very much used in medicine, resembles the preceding in external characters. It crystallises in cubes, and is very soluble in water. To prepare it, iodine is dissolved in a pure solution of potash, with the aid of heat, until the liquid begins to assume a permanent brownish yellow colour, indicating a slight excess of iodine. The liquid is now evaporated to dryness, and the dry residue ignited and melted in a covered platinum or iron vessel. The melted mass is poured out on a clean iron plate. It is iodide of potassium; and if dissolved in water and filtered, if necessary, the solution on evaporation yields pure crystals of the salt. In the first stage of this process, iodate of potash and iodide of potassium are formed: $I_6 + 6\,KO = 5\,KI + (KO, IO_5)$. In the second stage, the iodate is converted, by a red-heat, into iodide of potassium, oxygen being given off, while the iodide already present is unaltered: $5\,KI + (KO, IO_5) = 6\,KI + O_6$.

Another method is to form iodide of iron by bringing iron and iodine in contact under water. The iodide of iron dissolves, and the filtered solution is decomposed by an equivalent weight of carbonate of potash in solution: $Fe\,I + KO, CO_2 = KI + FeO, CO_2$. The insoluble carbonate of iron is separated by the filter, and the clear liquid evaporated till crystals are deposited.

Pure iodide of potassium is white, and dissolves entirely in hot alcohol. It is often adulterated with carbonate of potash, but that salt is easily detected by its insolubility in alcohol. The solution of iodide of potassium can dissolve a large quantity of free iodine, by which it acquires a deep brown colour. This solution is much used for baths; and the iodide is employed both externally and internally in scrofulous diseases.

Bromide of Potassium. $K\,Br = 117{\cdot}5$.

This salt is very analogous to the preceding, and is formed in the same way. It crystallises in cubes, and is very soluble in water. It has not been applied to any use.

Fluoride of potassium, $K\,F = 57{\cdot}8$, is obtained when hydrofluoric acid acts on potash. $HF + KO = HO + KF$. It is soluble and crystallises in cubes, and is very analogous to the preceding salts.

POTASSIUM AND SULPHUR.

Potassium combines with sulphur in several proportions, of which the most important are, the protosulphuret, KS, and the pentasulphuret, or persulphuret, KS_5.

Protosulphuret of Potassium. $KS = 55.2$.

This may be formed by melting together its constituents; but it is best prepared by passing hydrogen gas over neutral sulphate of potash, heated to bright redness. Here the hydrogen removes all the oxygen of the salt, and the sulphuret is left.

$$KO, SO_3 + H_4 = 4\,HO + KS.$$

Protosulphuret of potassium is a solid of a bright red colour, which forms with water a colourless solution. This solution smells of sulphuretted hydrogen, and probably contains that compound and potash, formed by the action of water on the sulphuret. $KS + HO = KO + HS$. The solution is alkaline, and if pure is decomposed by acids, without any separation of sulphur, sulphuretted hydrogen being given off.

Pentasulphuret or Persulphuret of Potassium. $KS_5 = 119{\cdot}5$.

This is the chief ingredient in what is called hepar sulphuris, or liver of sulphur, when prepared by fusing sulphur with carbonate of potash at the lowest possible temperature, when the persulphuret is formed along with hyposulphite of potash: $3\,KO + S_{12} = 2\,KS_5 + (KO, S_2\,O_2)$. Alcohol dissolves the sulphuret, which has a deep orange colour. It may be obtained pure in solution by boiling the protosulphuret with 4 eq. of sulphur and water. The persulphuret of potassium forms an orange or yellow solution, which is decomposed by acids, with the deposition of a large quantity, 4 eq. of sulphur.

There are 5 other compounds of sulphur and potassium, all similar in properties to the persulphuret. They are KS_2, KS_3, KS_4, $K_2\,S_7$, and $K_2\,S_9$. The last two are probably $(KS_2 + KS_5)$ and $(KS_4 + KS_5)$.

POTASSIUM AND SELENIUM.

The relations between these elements appear to be closely analogous to those between potassium and sulphur; but the compounds formed are little known.

POTASSIUM AND PHOSPHORUS.

These elements, when heated together, combine to form a solid phosphuret. When thrown into water, it gives rise to the disengagement of spontaneously inflammable phosphuretted hydrogen, while solid phosphuretted hydrogen separates, and hypophosphite of potash is found dissolved.

Nothing is known with certainty of the carburet of potassium, which is supposed by some to be formed in the process of making potassium.

No compound of potassium with silicon is accurately known: but with silicic acid potash forms compounds, which are known as glass. When the silica predominates, we have ordinary hard insoluble glass: when the potash is in excess, the compound is called silicate of potash. It is a glassy mass, soluble in water, and the solution has long been known as liquor of flints. (See, hereafter, under the head of Salts, the silicates, including glass and porcelain).

15. Sodium. Na = 23·3.

Syn. *Natrium.*—This metal is, perhaps, more abundant in our globe than any other; for it constitutes two-fifths of all the sea salt existing in sea water, in the water of springs, rivers, and lakes, in almost all soils, and in the form of rock salt. Sea salt is a compound of sodium with chlorine, $Na\,Cl$. Sodium also occurs as oxide of sodium, or soda, in a good many minerals; and more especially in the forms of carbonate, nitrate, and borate of soda: the first extracted from the soil in many parts of Africa; the second covering extensive plains in South America; and the third encrusting the shores of numerous lakes in Thibet. Soda is contained in sea plants, and in land plants growing near the sea, in the latter apparently replacing potash; it is the chief base in kelp, varec, or barilla, which are the ashes of sea-weed. Soda also occurs in most animal fluids.

Sodium is obtained by a process exactly similar to that above described for potassium, substituting acetate of soda for cream of tartar. Owing to the fortunate circumstance that sodium does not combine with carbonic oxide, the process is much more productive than in the case of the former metal. In fact, when properly conducted, we may expect to obtain the whole of the sodium. Thus, in the laboratory at Giessen, 1 lb. of calcined acetate of soda (carbonate containing a little charcoal) mixed with $\frac{1}{4}$ lb. of finely-powdered, and $\frac{1}{2}$ lb. of coarsely-powdered charcoal, and heated in a malleable iron bottle, as above recommended, yielded nearly 5 oz. of sodium, even when it was obvious that the result was capable of considerable improvement; the whole of the sodium present being about 7 oz. From the extreme cheapness of carbonate of soda, and the productiveness of the operation, sodium can be prepared far cheaper than potassium, and may, in most cases, be substituted for that metal, as its affinities are almost equally powerful. Should this metal be ever required on the large scale, it might be obtained for a price little, if at all, higher than that of zinc.

Sodium is a silver-white metal, having a very high lustre. It has not the bluish tinge of potassium, but, if any, rather a very slight yellowish tint, so that it resembles silver, while potassium resembles mercury. Its Sp. G. is 0·9348 ; it melts at 200°, being rather less fusible than potassium : but it is, on the other hand, somewhat more volatile, which is one cause of its preparation being easier, since it distils over at a lower heat.

SODIUM AND OXYGEN.

The affinity of sodium for oxygen is next to that of potassium. It rapidly attracts oxygen from the air, and must therefore be kept under naphtha ; but it is evidently less rapidly oxidised than potassium, and consequently keeps better. When heated in air or oxygen it takes fire, burning with a very pure and intense yellow flame, which is characteristic of sodium and of all its compounds. It decomposes water instantly, but does not spontaneously take fire when thrown on water, as potassium does. If the water, however, be thickened with gum, or if there be only a few drops of water, the action of sodium is attended with flame, and the yellow colour of the flame is most conspicuous. When exposed to the air, or burned in air or on water, sodium forms the protoxide, or soda: but it can form two other oxides—the suboxide and the peroxide. The suboxide is little known ; the peroxide is an orange powder, $Na_2\ O_3$. The only important oxide is the

Protoxide of Sodium. $Na\ O = 31{\cdot}313$.

Syn. *Soda.*—This oxide is formed when sodium is burned in dry air or oxygen. It is a white powder, which attracts moisture and carbonic acid from the air. When sodium is oxidised by water, or when the protoxide is dissolved in water, there is formed the true alkali, the hydrated oxide of sodium, or hydrate of soda, $Na\ O,\ H\ O$.

Syn. *Caustic Soda.*—This hydrate is prepared by a process exactly similar to that given for caustic potash, substituting carbonate of soda for carbonate of potash. If the carbonate of soda be in crystals, 1 part of quick lime is sufficient for 5 or 6 parts of carbonate: if dry, 1 part of quick lime will suffice, if pure, for 2 of carbonate. As the lime is seldom pure, it is in general safer to take 2 parts for 3 of dry carbonate of soda.

The solution of caustic soda, owing to the superior purity of the carbonate, which is generally free from sulphate and chloride, is much purer than the common aqua potassæ: and when boiled down, it leaves a very pure hydrate of soda, NaO, HO. This hydrate is, in all external characters, and in most chemical ones, exactly similar to caustic potash: it is deliquescent and caustic, and may be used for almost all the same purposes. The solution, however, cannot be used for organic analysis, as it froths up like solution of soap when a gas passes through it.

With acids soda forms salts, all of which, with hardly an exception, are soluble in water, and many of which crystallise. The solubility of its salts serves to distinguish soda from potash, for neither bichloride of platinum, tartaric acid, perchloric acid, nor carbazotic acid causes any precipitate in the salts of soda, even when alcohol is added. Hydrofluosilicic acid is the only test that forms a precipitate in cold and pretty strong solutions of soda salts; but the silicofluoride of sodium, thus formed, is much more soluble than the corresponding salt of potassium. When we know that either potash or soda is present, and the tests give the above negative results, we may safely decide on the presence of soda; but if we wish for positive evidence, this can only be obtained by setting fire to alcohol along with the suspected salt, or exposing the salt on platinum wire to the flame of the blowpipe; when, if soda be present, a rich and pure yellow colour will be given to the flame.

The chief uses of soda are in the manufacture of glass and of hard soap. The carbonate is used in washing, and is a powerful detergent, although milder than carbonate of potash.

SODIUM AND CHLORINE.

Chloride of Sodium. $NaCl = 58{\cdot}75$.

SYN. *Muriate of Soda.—Sea Salt.—Rock Salt.—Kitchen Salt.*—This very important salt is formed when chlorine and sodium, or hydrochloric acid and soda, come together. But it is found in immense quantity, dissolved in sea water, and in the water of salt springs, and in smaller quantity in all natural waters, by which, indeed, it is carried to the sea, where it accumulates. Inland seas, without any outlet, and where, consequently, the superfluous water escapes only by evaporation, become more saline than sea water, although the streams which feed them are not richer in salt than ordinary rivers. Hence the Dead Sea in Palestine, fed by the Jordan, is a very strong brine, containing the same ingredients as sea water, but far stronger; these ingredients being also the same which are found in the Jordan and all rivers, in much smaller quantity. Salt is also found abundantly, as rock salt, in various countries. It is obtained from the sea water by simple evaporation, either spontaneous, or with the aid of heat, till crystals separate, which are nearly pure chloride of sodium.

The properties of salt are well known. It is singular that it is not materially more soluble in hot than in cold water, for which reason it separates in crystals from the hot liquid during evaporation, and ought to be taken out from time to time with a perforated ladle, to allow the mother liquor to drain off.

One chief use of salt is as an antiseptic in curing meat. It seems to act chiefly by removing so much water from the flesh that too little is left to allow of putrefaction. Hence, highly salted meat is always dry, and requires long steeping in water to render it eatable. Salt is also employed to yield hydrochloric (muriatic) acid, and chlorine, for the making of bleaching-powder, as well as the best carbonate of soda. In preparing hydrochloric acid from salt, which is done by the aid of oil of vitriol, sulphate of soda is formed, from which, by heating it with charcoal, carbonate of soda is obtained. Thus, in the very important manufacture of soda from salt, both the chlorine and the sodium are made use of; the hydrochloric acid being but a secondary product, formed in the first stage of the manufacture of carbonate of soda, a product nearly equal in importance to the oil of vitriol, by means of which it is made.

But the most important use of salt, which renders it an absolute necessary of life to animals in some shape or other, is as a condiment to food, or rather, as a substance indispensable to digestion. This subject will be fully treated of in the Second Part of this work: in the meanwhile, it may be mentioned, that the free muriatic acid, always present in the chyme before it leaves the stomach, and the soda which is found in the chyle and in the blood, and which is the essential basic element of the bile, are both derived from salt, either originally present in the food, or, as is most commonly the case, added to it by man. Herbivorous animals, who produce an enormous quantity of bile, find salt in their food, and above all in the river or spring-water they drink. But they are so sensible of the good effects of salt, that they show the greatest preference for salt springs, and indeed for solid salt, if placed within their reach. When supplied with salt in moderate quantity, they thrive uncommonly well, as in salt marshes, which are well known to give rise to very rich and well-feeding pastures. An excess of salt is, however, injurious.

SODIUM WITH BROMINE, IODINE, AND FLUORINE.

The compounds of sodium with these elements are quite analogous to those of potassium above described. The iodide and bromide of sodium are found in sea-water and in salt springs, in minute quantity. The formulæ of these three compounds are $Na\ Br$, $Na\ I$, and $Na\ F$.

SODIUM WITH SULPHUR.

Sodium, like potassium, unites with sulphur in several proportions. The protosulphuret, $Na\ S$, is very similar to the corresponding sulphuret of potassium; the others are little known.

It is very remarkable that the beautiful mineral, lapis lazuli, or ultra-marine, the nature of the colouring matter in which was long a complete puzzle to chemists, should, according to recent discoveries, owe its magnificent blue colour to the presence of sulphuret of sodium, a compound destitute of any such colour. But this seems to be really the case: for by heating a mixture of hydrated alumina and silicic acid to whiteness, along with sulphuret of sodium, C. G. Gmelin has succeeded in preparing artificial ultra-marine, which is now prepared in France quite equal to the native pigment, and very much cheaper. We are still quite in the dark as to the true nature of the blue compound formed in this operation.

The compounds of sodium with phosphorus, carbon, boron, and silicon are unknown. With silicic acid, soda, like potash, forms glass.

16. Lithium. $L=6{\cdot}42$.

This metal is very rare, occurring only as oxide or lithia in a few rare minerals, such as spodumene, petalite, lepidolite, and lithion-mica. The metal has been obtained in small quantity by means of galvanism from the oxide, and is white, burning when heated, with a blood-red flame, and forming protoxide of lithium, or lithia.

Protoxide of Lithium. $LO=14{\cdot}43$.

This alkali can only be obtained from either of the above minerals, which are silicates. One part of the mineral in fine powder is mixed with two of fluor-spar, and the mixture heated with sulphuric acid, until the whole of the silica is dissipated. There then remains a mixture of sulphates of alumina, lime, and lithia, and, in the case of lepidolite or spodumene, potash. By boiling with carbonate of ammonia in excess, the alumina and lime are precipitated, and the filtered liquid is evaporated to dryness, and ignited to expel the sulphate of ammonia. The residue is sulphate of lithia, or sulphates of lithia and potash. In the latter case, by the cautious addition of chloride of barium, the sulphuric acid is separated as sulphate of baryta, and the lithia and potash converted into chlorides. These being dried, are digested in absolute alcohol, which dissolves the chloride of lithium. The lithia is now free from other bases: to obtain it in the separate state, the chloride is converted into sulphate, by being boiled with oil of vitriol, and the solution of the sulphate decomposed by the exact equivalent of barytic water, by which the sulphuric acid is precipitated, while the free lithia is dissolved, and the solution, if evaporated, leaves hydrate of lithia, LO, HO.

Lithia is not quite so soluble in water as soda or potash, nor is it so caustic; but it very much resembles these alkalies. Its solution attracts carbonic acid as readily as theirs from the atmosphere. When lithia is fused on platinum, it corrodes and stains the metal. Lithia and all its salts give a blood-red colour to flame. The carbonate of lithia is sparingly soluble, and its phosphate is nearly insoluble. Lithia occurs too rarely to admit of any useful application; but it is important to know that lithion-mica, which is recognised by its easy fusibility before the blow-pipe, and by its tinging the outer flame red, has hitherto been only found associated with albite and topaz, or pycnite, in tin districts, and its occurrence, thus associated, may be looked on as a sure indication of the existence of tin in the locality.

Chloride of lithium, L Cl, crystallises in cubes. It is very deliquescent and soluble in alcohol, the flame of which it colours of a fine red.

Appendix to the First, or Alkaline Group of Metals.

Ammonium. $NH_4 = Am = 18{\cdot}19$.

This hypothetical compound metal has already been described under the head of Ammonia, but we must here considered it as a metal, analogous to the three just described.

In all the salts of ammonia with oxygen acids Am O is found.

This compound, oxide of ammonium $= NH_3$, HO, is itself a very powerful and caustic alkali, and neutralises all the acids. It is important to observe that it is isomorphous with potash, KO; so that the salt KO, SO_3 has the very same form as Am O, SO_3.

Chloride of Ammonium. Am $Cl = NH_4 Cl = NH_3$, H $Cl = 53{\cdot}64$.

This is the well-known salt, sal ammoniac, which is analogous to K Cl, Na Cl, and L Cl, crystallising, like them, in cubes. It is the salt from which ammonia and all its compounds are formed, and it is prepared from the impure carbonate of ammonia obtained by distilling animal matters. It is entirely volatile, soluble in water, has a pungent saline taste, and no smell. Its chemical relations are those of a chloride, although it is called muriate of ammonia, because it is formed when muriatic (hydrochloric) acid and ammonia act on each other. But there is little doubt that these bodies mutually decompose each other, according to the equation, $NH_3 + HCl = NH_4, Cl$.

The bromide, iodide, and fluoride of ammonium are very similar to the chloride.

ORDER 2.—METALS OF THE ALKALINE EARTHS.

17. BARIUM. $Ba = 68{\cdot}7$.

This metal may be obtained with difficulty, by causing the vapour of potassium to pass over baryta (oxide of barium) strongly heated in an iron tube. The potassium is oxidised at the expense of the barium, forming potash, while barium is separated. $Ba O + K = KO + Ba$. Mercury dissolves out the barium forming a fluid amalgam, and this, if the mercury is distilled off in a small iron retort, leaves the barium.

Barium is a metal of a dark grey colour, heavier than oil of vitriol. When exposed to the air it rapidly absorbs oxygen, forming a white powder, the protoxide of barium or baryta. It is also oxidised by water, hydrogen being liberated.

Protoxide of Barium. $Ba O = 76{\cdot}713$.

SYN. *Baryta.*—This alkaline earth occurs in nature combined with carbonic and sulphuric acids. It is best obtained pure by decomposing pure nitrate of baryta, by a continued red-heat, when the nitric acid is destroyed, being expelled as nitrous acid and oxygen, and the baryta left behind. $Ba O, NO_5 = Ba O + NO_4 + O$.

Baryta is a grey porous solid, the Sp. G. of which is about 4·000. It has an acrid alkaline taste, but is much less soluble in water than potash or soda. When sprinkled with water, it slakes, like quicklime, combining with the water to form a dry, white powder, hydrate of baryta. Great heat attends this combination. Baryta, if exposed to the air, speedily attracts moisture and falls to powder, and the hydrate absorbs carbonic acid from the air, and is converted into carbonate by degrees.

Hydrate of Baryta. $BaO, HO = 85{\cdot}726$.

This compound is formed when dry baryta is slaked with water, as above mentioned. It is a bulky white powder, which dissolves in 3 parts of boiling water, and in about 20 of cold water. The saturated hot solution deposits, on cooling, crystals, which are composed of $BaO, HO + 9\,aq$. The saturated cold solution, which is called barytic water, is a most useful test of the presence of carbonic acid in the air, or in any gas; for with that acid it instantly produces the insoluble carbonate of baryta, which forms a film, or crust, on the liquid.

A solution of baryta may be formed, extemporaneously, by boiling sulphuret of barium in solution with oxide of copper or oxide of lead in excess, and filtering as soon as the liquid gives a white, and not a black precipitate with acetate of lead. The change is as follows: $BaS + CuO = BaO + CuS$; or $BaS + PbO = BaO + PbS$. The sulphurets of lead and copper, being insoluble, are easily separated by the filter.

Baryta may be recognised, either in the free state, or in its salts, by its giving, with alkaline carbonates, a white precipitate of carbonate, and with sulphuric acid or any soluble sulphate, a white precipitate of sulphate of baryta. The latter is quite insoluble in water and acids; and hence baryta and its salts are much used as tests for sulphuric acid.

Peroxide of Barium. $BaO_2 = 84{\cdot}7$.

This oxide is formed either by passing oxygen over baryta at a red-heat, or by sprinkling chlorate of potash on baryta heated to very low redness, and washing away the soluble part with water. In the latter case it is obtained as a hydrate. It is insoluble in water, and weak acids dissolve it, forming a salt of protoxide; while the oxygen combines with water, forming a peroxide of hydrogen. In fact, the peroxide of barium is only used for the purpose of making that compound.

BARIUM AND CHLORINE.

Chloride of Barium. $Ba\,Cl = 104{\cdot}17$.

This salt is best obtained by dissolving carbonate of baryta in hydrochloric acid, $Ba\,O,CO_2 + H\,Cl = Ba\,Cl + HO + CO_2$. It is also obtained by acting on solution of the sulphuret of barium with the same acid, $Ba\,S + H\,Cl = Ba\,Cl + HS$. In the former case carbonic acid gas, in the latter sulphuretted hydrogen gas, is disengaged; and in both the chloride of barium remains dissolved, and, on evaporation, crystallises in white brilliant tabular crystals, which are composed of $Ba\,Cl + 2\,aq$. A red-heat expels the water of crystallisation, and chloride of barium is left.

It is a white solid, soluble in water, and is used in medicine, and very extensively in chemistry, as a test for sulphuric acid, and a means of removing that acid from any solution.

Bromide, iodide, and fluoride of barium are very analogous to the chloride.

BARIUM AND SULPHUR.

Sulphuret of Barium. $Ba\,S = 84{\cdot}82$.

This useful compound, from which all the other compounds of barium may be obtained, is prepared from the native sulphate of baryta, or heavy spar, by reducing it to fine powder, mixing it with $\frac{1}{6}$ of its weight of lamp black (charcoal), and exposing the mixture to a white heat for two hours in a covered crucible. The following change takes place—

$$Ba\,O, S\,O_3 + C_4 = 4\,C\,O + Ba\,S.$$

The sulphuret of barium dissolves in hot water, forming a colourless solution, which, if exposed to the air, gradually absorbs oxygen, becoming yellow, and is finally converted into hyposulphite of baryta, the latter salt being deposited in hard brilliant crystals. When, in preparing the sulphuret, the heat has been insufficient, the sulphuric acid of the sulphate of baryta is entirely deoxidised, the baryta only partially, and we obtain a mixture of baryta and persulphuret of barium, $Ba\,S_2$. Thus $2\,(BaO,SO_3) + C_8 = C + 7\,CO + Ba\,O + Ba\,S_2$. This mass, dissolved in hot water, deposits, on cooling, crystals of hydrate of baryta: while the solution, owing to the presence of persulphuret, is orange-coloured.

Sulphuret of barium, from its solubility, and from its being easily decomposed, serves to prepare all the compounds of barium. This, as already stated, if boiled with oxide of copper or of lead, yields hydrate of baryta; and oxide of manganese may be used for the same purpose. With hydrochloric acid it yields chloride of barium, and with nitric or acetic acid it gives rise to nitrate or acetate of baryta, $Ba\,S + HO, NO_5 = HS + Ba\,O, NO_5$. Mixed with carbonate of potash, soda, or ammonia, in solution, it produces insoluble carbonate of baryta, and a soluble sulphuret of potassium, sodium and ammonium, $Ba\,S + KO, CO_2 = KS + BaO, CO_2$. From the nitrate pure baryta, and from the carbonate, any salt of baryta may be obtained.

All the compounds of barium, except the sulphate, are poisonous.

18. Strontium. $Sr = 43{\cdot}8$.

Oxide of Strontium. $Sr\,O = 51.813$.

This metal is analogous to barium, but little known. It occurs only as oxide, combined with carbonic acid in Strontianite, and with sulphuric acid in celestine. From these minerals the oxide of strontia may be obtained, by processes exactly similar to those described for baryta. Strontia is rather less soluble in water than baryta, but otherwise much resembles it. Indeed it was long confounded with baryta, from which it is distinguished by forming with hydrochloric acid a chloride which crystallises in needles, and is very deliquescent and soluble in alcohol, to which it gives the property of burning with a crimson flame. The nitrate of strontia is used in making the red fire of the theatres, which is also employed for signal lights.

The chloride and sulphuret of strontium are prepared as those of barium, and from the latter, hydrate of strontia and all the salts of strontia may be prepared. The sulphate of strontia is not absolutely insoluble, like that of baryta, although it is very nearly so.

19. Calcium. $Ca = 20{\cdot}5$

Oxide of Calcium. $Ca = 28{\cdot}513$.

This metal is little known, but it appears to resemble the two preceding. It is soon oxidised in air or in water, forming the oxide of calcium, or quicklime.

The oxide, or lime, occurs in great abundance in nature chiefly as carbonate, in the forms of marble, limestone, chalk and calcareous spar; also as sulphate, in the shape of gypsum and alabaster. Carbonate of lime is the chief ingredient of shells, and phosphate of lime is the earthy part of bones. Lime is found in the ashes of many plants.

Pure lime is easily obtained by igniting white marble or chalk till all the carbonic acid is expelled. The residue is seldom quite white, but combines with water to form a snow-white hydrate (slaked lime). A high temperature is produced in the slaking of lime. Lime is far less soluble in water than baryta or strontia, and cold water dissolves a good deal more lime than hot, about $\frac{1}{500}$. The solution is called lime water; it tastes acrid, and if exposed to the air, is soon covered with a film of carbonate, which forms a crust that at length breaks. Quicklime, exposed to air, gradually absorbs both water and carbonic acid; but a good red heat always restores it to the state of quicklime again. When an excess of hydrate is mixed up with water, it forms a milky-looking fluid, called milk or cream of lime, which is much used for absorbing carbonic acid.

The uses of lime are well known: slaked lime is the chief ingredient in mortar, and lime water is used in medicine as an antacid. With acids lime forms salts, of which the carbonate, like that of baryta or strontia, is insoluble, the chloride very deliquescent, and the sulphate sparingly soluble, but far from insoluble. Lime and its salts are recognised by forming, with oxalate of ammonia, the very insoluble oxalate of lime. In testing for lime, the solution must be neutral, as an excess of acid dissolves the oxalate.

Chloride of Calcium. $Ca\,Cl = 55{\cdot}97$.

This salt is formed when carbonate of lime is dissolved in hydrochloric acid, as in preparing carbonic acid gas, $Ca\,O, CO_2 + H\,Cl = Ca\,Cl + H\,O + CO_2$. When the neutral solution is evaporated to the consistence of syrup, it forms, on standing in a cold place, long prisms of crystallised chloride of calcium, $Ca\,Cl + 2\,HO + 4\,aq$. At 480° these lose the 4 equivalents of water of crystallisation, and at a red-heat the other two equivalents of water. The crystals, when powdered and mixed with snow, liquefy rapidly, and produce intense cold. In every form chloride of calcium has a great attraction for water, and it is much used for drying gases, and in organic analysis for collecting the water, by weighing which the proportion of hydrogen is determined. It also serves to deprive alcohol, ether, and many similar fluids, of water.

The bromide and iodide of calcium are deliquescent salts, $Ca\,Br$ and $Ca\,I$.

Fluoride of Calcium. $Ca\,F = 39{\cdot}24$.

This is a very abundant mineral, occurring chiefly in veins along with lead ore, heavy spar, and quartz. It is well known as fluor, or Derbyshire spar, and crystallises beautifully in cubes, octahedrons, and tetrahedrons, which are transparent and colourless, or purple, green, brown, or yellow. It also occurs in a massive semi-crystalline form, capable of being cut and polished for ornaments. It is very remarkable that fluoride of calcium is an ingredient of bones in variable quantity. It is said to be found chiefly in the enamel of the teeth, and it is certainly found in variable quantity, but always present, in ancient human bones. It is now said that it is less easily detected in recent bones, owing to the presence of animal matter. It has been found in some bones to the amount of 10 per cent.

The presence of it is detected by treating the mineral or bone, after ignition, with oil of vitriol in a platinum crucible, covered with a waxed plate of glass, having the glass exposed by traces made with a point through the wax. In a short time the traces are so far etched as to be indelible, and very small traces of fluor spar may be thus detected.

Sulphuret of Calcium. $CaS = 36{\cdot}62$.

This compound is formed by a process similar to that given for sulphuret of barium. Sulphate of lime, mixed with $\frac{1}{4}$ of its weight of charcoal powder, is strongly ignited for an hour or two in a covered crucible. $CaO, SO_3 + C_4 = 4\,CO + CaS$.

It is a nearly white powder, provided no excess of charcoal is present, and is very sparingly soluble in water. When it has been exposed to the sun's rays, it shines in the dark, and is called Canton's phosphorus. When water, lime, and sulphur are boiled together, there is formed a yellow or orange solution containing hyposulphite of lime and persulphuret of calcium. This liquid, acted on by hydrochloric acid, yields persulphuretted hydrogen. When sulphur and lime are melted together, there is formed a mixture of sulphate of lime and sulphuret of calcium.

Phosphuret of calcium is obtained, in an impure state, by bringing phosphorus in contact with red-hot lime. A brown powder is formed, which is a mixture of phosphate of lime and phosphuret of calcium. When thrown into water it produces spontaneously inflammable phosphuretted hydrogen, along with hypophosphite and phosphate of lime.

20. MAGNESIUM. $Mg = 12{\cdot}7$.

This metal is obtained by causing the vapour of potassium to come in contact with red-hot chloride of magnesium in a tube. Vivid incandescence takes place, chloride of potassium is formed, and magnesium separated. When the mass is acted on by cold water, the chloride dissolves and the magnesium is left in globules.

Magnesium is silver-white, very brilliant and malleable. It melts at a red-heat; and if heated in air or oxygen, burns vividly, being converted into oxide of magnesium, or magnesia. It does not decompose water, even when boiled with it; and is not oxidised at ordinary temperatures by dry air. Hence it may be preserved far more easily than any of the preceding metals. It dissolves in diluted acids, hydrogen being disengaged.

MAGNESIUM AND OXYGEN.

Oxide of Magnesium. $MgO = 20{\cdot}713$.

Syn. *Magnesia; Calcined Magnesia.*—This oxide occurs in nature as carbonate, forming considerable masses of rock in some parts of the world; also as a mixed carbonate of lime and magnesia, under the forms of dolomite and magnesian limestone; and as sulphate of magnesia, or Epsom salts, which occurs in many saline springs.

It is best obtained pure by heating the carbonate to redness. Pure or calcined magnesia is a bulky white powder, insoluble in water. It has an earthy taste, and readily unites with acids, neutralising them, on which account, and because it is in itself mild in its action, it is much used in medicine as an antacid. Magnesia, when precipitated from its salts by an alkali, combines with water, forming a hydrate, MgO, HO, which loses its water in a low red-heat. This hydrate is found native, crystallised.

Of the salts of magnesia, the carbonate, like that of the three preceding earths, is insoluble; but the sulphate is very soluble. The solution of this, or any other soluble salt of magnesia, is precipitated by potash, soda, and ammonia, which throw down pure magnesia; and by carbonates of potash and soda, which form carbonate of magnesia. But carbonate of ammonia causes no precipitate, owing to the formation of a soluble double salt; and for the same reason, oxalate of ammonia does not precipitate the salts of magnesia. By this last character magnesia may be distinguished and separated from lime. The most delicate test of magnesia in solutions is to add, first, carbonate of ammonia, and then phosphate of soda, which then forms an insoluble double phosphate of ammonia and magnesia, in the form of a heavy crystalline powder, slowly formed when the quantity of magnesia is very small.

Besides its uses in medicine, magnesia is a useful ingredient of all fertile soils. The double phosphate of ammonia and magnesia is found in the husk of grain, and in the potato; and phosphate of magnesia is also found in bones. In a soil totally destitute of magnesia, grain does not produce perfect seed, however well the plants may thrive or grow in the stalk or leaf, to which parts magnesia seems not to be essential. Owing to the occurrence of the double phosphate in potatoes, bran, which contains that salt, is a very powerful manure for that crop.

MAGNESIUM WITH CHLORINE, BROMINE, IODINE, AND FLUORINE.

Chloride of Magnesium. $Mg\,Cl = 48{\cdot}17$.

This salt is best formed as follows:—Take two equal portions of hydrochloric acid, and neutralise one with magnesia, the other with ammonia; then mix, evaporate to dryness, and ignite in a covered crucible till the sal ammoniac is dissipated. Fused chloride of magnesium remains, which is poured out on a clean stone, and when solidified kept in a closely-stopped bottle. It is highly deliquescent, and is used for preparing magnesium.

When magnesia acts on hydrochloric acid, they combine, producing hydrochlorate of magnesia, $Mg\,O, H\,Cl$, a rare case. On evaporating the solution to dryness and heating it, hydrochloric acid is expelled and magnesia is left. But when sal ammoniac is added (chloride of ammonium, $N\,H_4, Cl$), and the mixture evaporated, chloride of magnesium is formed, and unites with the sal ammoniac, forming a double chloride, $Mg\,Cl + N\,H_4, Cl$. When this is ignited, the sal ammoniac is expelled, and chloride of magnesium is left. Chloride of magnesium exists in sea water, and is found in the mother liquor of the crystals of salt.

The iodide and bromide of magnesium are very soluble; the fluoride is insoluble.

Sulphuret of magnesium may be obtained by a method similar to that given for sulphuret of barium. When pure, it is a white brittle mass, partially soluble in water.

ORDER 3.—METALS OF THE EARTHS PROPER.

21. ALUMINUM. $Al = 13{\cdot}7$.

This metal is best obtained, like the last, by the action of potassium on the chloride. Chloride of aluminum is mixed with small fragments of potassium in a platinum crucible, the lid of which is wired down. Heat is then applied by means of a spirit-lamp, when a violent action ensues, and a dark grey mass is left, from which water dissolves chloride of potassium, leaving aluminum as a grey powder, which has considerable lustre. It is not easily melted; and when heated in the air, or in oxygen gas, it burns with a vivid light, forming alumina, which is a sesquioxide of the metal.

ALUMINUM AND OXYGEN.

Sesquioxide of Aluminum. $Al_2 O_3 = 51{\cdot}539$.

SYN. *Alumina; Pure Clay.*—This earth is very abundant in nature. It occurs crystallised as the sapphire and ruby; in a crystalline, but more massive form, as corundum or emery; and as the chief ingredient of all clays, and of most slaty rocks, from which, indeed, clays are derived. Pipe-clay is the purest clay, but is not pure alumina, although approaching to it.

Pure alumina is best prepared as follows:—A solution of alum is precipitated by an excess of chloride of barium, by which means the sulphuric acid is separated, and chloride of aluminum is left in solution with the chloride of potassium and the excess of chloride of barium. Alum ($K O, SO_3 + Al_2 O_3, 3 SO_3$) with $4 Ba Cl$ yields $4 (Ba O, S O_3) + K Cl + Al_2 Cl_3$. On evaporation, water is decomposed, and hydrochlorate of alumina is formed, $Al_2 Cl_3 + 3 H O = Al_2 O_3, 3 H Cl$. When the dry mass is ignited, the hydrochloric acid is expelled, and the alumina is left with the chlorides of potassium and barium, which are removed by water.

Pure alumina is a fine white powder, quite unalterable in the fire. When precipitated from its solution in acids by alkalies, it forms a very bulky gelatinous hydrate, which, when dried at 60°, is $Al_2 O_3, 6 H O$; if dried at 100° it becomes $Al_2 O_3, 3 H O$. Dry or anhydrous alumina, mixed with water, forms a plastic mass, which admits of being moulded. This property is given to clay by the presence of alumina, and is the foundation of the art of making porcelain or earthenware.

Alumina, after ignition, is almost insoluble in acids; but the hydrate readily dissolves in all strong acids, forming salts which have a peculiar astringent taste.

Alumina is precipitated, as hydrate, from its solutions by potash, soda, ammonia, and their carbonates; but the precipitate readily dissolves in an excess of the two first. Hydrosulphuret of ammonia, which precipitates none of the previously-described metallic oxides, causes in solutions of alumina a precipitate, which, however, is not a sulphuret, but the hydrate of alumina precipitated by the ammonia of the test.

Besides the use of alumina in pottery, it is much used in dyeing and calico-printing, from its attraction for vegetable colouring matters, and for the fibre of cloth. It forms a bond of union between the cloth and the dye, and fixes the latter on the former. It is said, in this, to act as a mordant, and is most generally used in the shape of alum or acetate of alumina. When solution of alum is mixed with a colouring matter, and the alumina then precipitated by an alkali, the hydrate carries with it all the colouring matter, or the greater part of it, and forms what is called a lake. The water colour termed lake is merely a lake made with some pink dye stuff, such as madder or logwood. Carmine is a lake of cochineal.

ALUMINUM AND CHLORINE.

Sesquichloride of Aluminum. $Al_2\ Cl_3 = 133{\cdot}81$.

This compound is prepared by passing chlorine gas over a mixture of alumina and charcoal, heated to redness in a tube. The chloride sublimes into the cold part of the apparatus. It forms a volatile crystalline mass, colourless or slightly yellow. It fumes in the air, and dissolves in water with much heat. It appears at first to combine with the water, forming a hydrated chloride, $Al_2\ Cl_3,\ 3\ HO$; but on heating this, hydrochloric acid is expelled, and alumina is left, $Al_2\ Cl_3,\ 3\ HO = Al_2\ O_3,\ 3\ H\ Cl$. The chloride is used for the preparation of aluminum.

The sulphuret of aluminum is formed when sulphur is dropped on red-hot aluminum. It is a dark grey mass, which decomposes water, forming sulphuretted hydrogen and alumina, and hence its composition must be $Al_2\ S_3$. If so, we have $Al_2\ S_3 + 3\ HO = Al_2\ O_3 + 3\ H\ S$. Similar compounds are formed with phosphorus and selenium.

22. Glucinum. 23. Yttrium. 24. Thorinum. 25. Zirconium.

These metals, or rather their oxides, are all so rare as not to admit of any useful application. The oxides, which are glucina, yttria, thorina, and zirconia, only occur in a few rare minerals.

Glucina occurs in the emerald and the beryl. Its composition is analogous to that of alumina; and its formula is $G_2\ O_3$. It is a white powder, insoluble in water, soluble in acids, forming salts which have a sweetish taste. It resembles alumina very much, but differs from it in being soluble in solution of carbonate of ammonia. The metal, which may be obtained, like aluminum, from the chloride, burns with amazing splendour when heated in oxygen.

Yttria, the oxide of yttrium, occurs in gadolinite, in yttrocerite, and in yttrotantalite. The pure earth is a white powder, which dissolves in acids, forming sweetish salts, from which yttria is precipitated by alkalies; but is not, like alumina and glucina, redissolved by excess of potash or soda. It is, moreover, precipitated by ferrocyanide of potassium, which these earths are not. Yttria seems to be a protoxide of yttrium, $Y\,O$. The salts of yttria have often an amethyst colour; but the recent researches of Mosander seem to show that this is owing to the presence of the oxide of one of the new metals detected by him, which accompany yttrium. It is probable that pure yttria is not yet known.

Thorina is still more rare, and has only been found in one mineral—thorite. It is a white powder, resembling yttria. The metal, thorinum, burns in air or oxygen, when heated, with great splendour. It also burns with sulphur and phosphorus, as do the two preceding metals.

Zirconia is found in the zircon or hyacinth. It resembles alumina in appearance. It differs from all the preceding earths in being precipitated as an insoluble subsulphate, when solutions of its salts are boiled with sulphate of potash. The metal, zirconium, resembles aluminum. The oxide is believed to be a sesquioxide $Zr_2\,O_3$.

METALS.—CLASS II.

ORDER 1.—METALS, THE PROTOXIDES OF WHICH ARE POWERFUL BASES, BUT WHICH DO NOT DECOMPOSE WATER, UNLESS WITH THE AID OF A RED-HEAT.

26. MANGANESE. $Mn = 27{\cdot}7$.

This metal occurs in considerable abundance, chiefly as deutoxide or peroxide $Mn\,O_2$, which is much used in the arts and in chemical manufactures, as well as in the laboratory. The metal is obtained by making oxide of manganese into a paste with oil, and exposing this paste to a strong white-heat in a covered crucible. If the heat be high enough, a button of the metal is obtained.

It is a hard, brittle, very difficultly fusible metal, of a greyish white colour, Sp. G. 8·013. It tarnishes on exposure to the air, and is rapidly oxidised when heated. It decomposes water rapidly at a red-heat, hydrogen being disengaged. As a metal, it is not applied to any useful purpose.

MANGANESE AND OXYGEN.

a. Protoxide of Manganese. $Mn\,O = 35{\cdot}713$.

This oxide is obtained when the peroxide is acted on by hydrogen gas at a red-heat. But the best method is to heat to redness a mixture of 1 part of dry chloride of manganese, 1 part of sal-ammoniac, and 2 parts of dry carbonate of soda. The chloride acts on the soda, $Mn\,Cl + Na\,O = Mn\,O + Na\,Cl$; forming oxide of manganese and chloride of sodium: while the carbonic acid escapes as gas: the sal-ammoniac is also expelled, and its vapour serves merely to exclude the oxygen of the atmosphere. From the fused mass, water extracts the chloride of sodium; and leaves the protoxide of manganese undissolved.

It is a powder of a pale grass green colour, which, if prepared by hydrogen at a low red-heat, soon attracts oxygen from the air and becomes brown. If it has been made, however, at an elevated temperature, especially by the second process, it is more compact, and keeps tolerably well. When heated in the air, it takes fire and burns.

Protoxide of manganese is a powerful base, neutralising acids and forming salts, which are either colourless or have a tinge of flesh colour. Its solutions give, with caustic alkalies, a precipitate of hydrate, which is at first white, but soon absorbs oxygen and becomes brown; with carbonated alkalies, a white precipitate of carbonate of manganese, which retains its whiteness till it is dried, when it becomes generally slightly fawn-coloured. Hydrosulphuret of ammonia causes a flesh-coloured precipitate of sulphuret of manganese, which, in the air, absorbs oxygen and becomes brown. Chloride of soda or bleaching liquor causes a bulky dark-brown precipitate of hydrated peroxide. The two last tests are characteristic. Ferrocyanide of potassium gives a white precipitate. All the salts of protoxide of manganese may easily be prepared from the carbonate, which again is most economically made from the chloride, the preparation of which will be described below. The sulphate is used in calico-printing.

b. Sesquioxide of Manganese. $Mn_2\,O_3 = 79{\cdot}439$.

This oxide is left behind when the peroxide is ignited in preparing oxygen gas. $2\,Mn\,O_2 = Mn_2\,O_3 + O$. It is a dark-brown powder, very similar to the peroxide, but rather lighter in colour, and yielding no oxygen when ignited. It is a feeble base, and is only known to combine with sulphuric acid, forming an amethyst-coloured solution of sesquisulphate. With sulphates of potash and ammonia, this salt forms manganese alums, which crystallise in dark purple octahedrons. When heated with sulphuric acid, it yields oxygen, and with hydrochloric acid, chlorine, but less of either than the peroxide, which see. As some specimens of peroxide are, naturally or accidentally, mixed with sesquioxide, the manufacturer finds it a source of inconvenience and loss. It occurs in a pure state as braunite, and combined with baryta in psilomelan. Its hydrate is the mineral manganite. Its powder is dark brown.

c. Hyperoxide or Peroxide of Manganese. $\mathrm{Mn\,O_2} = 43{\cdot}726$.

SYN. *Deutoxide of Manganese.*—This oxide is found in considerable abundance, and is known in the mineral kingdom as pyrolusite. It generally assumes the form of a black shining mass composed of radiated groups of acicular crystals; also in distinct crystals, which are right rhombic prisms; and in the compact and even earthy state. Its powder is black. When heated to redness, it loses one-fourth of its oxygen, leaving sesquioxide; $2\,\mathrm{Mn\,O_2} = \mathrm{Mn_2\,O_3} + \mathrm{O}$. In a white-heat it is said to lose half its oxygen, leaving protoxide. Heated with oil of vitriol, it forms sulphate of protoxide, and half the oxygen is expelled. $\mathrm{Mn\,O_2} + \mathrm{HO, SO_3} = (\mathrm{Mn\,O, HO, SO_3}) + \mathrm{O}$. With hydrochloric acid it yields chlorine, chloride of manganese, and water. $\mathrm{Mn\,O_2} + 2\,\mathrm{H\,Cl} = \mathrm{Cl} + \mathrm{Mn\,Cl} + 2\,\mathrm{H\,O}$. It also yields chlorine when heated with common salt and sulphuric acid; and this is the process commonly used by the manufacturers of bleaching powder. $\mathrm{Mn\,O_2} + \mathrm{Na\,Cl} + 2\,\mathrm{HO, SO_3} = (\mathrm{Mn\,O, HO, SO_3}) + (\mathrm{Na\,O, HO, SO_3}) + \mathrm{Cl}$.

It is further used in glass-making to destroy the colour given to the glass by protoxide of iron, which it converts into peroxide; in larger proportion, to give glass an amethyst colour; and in numerous operations in the laboratory as a convenient oxidising agent.

With water, peroxide of manganese forms a hydrate, $\mathrm{MnO_2, HO}$, which is obtained when salts of the protoxide are acted on by bleaching liquor, or when the acids of manganese are spontaneously decomposed. It is a beautiful brown powder, which is decomposed by heat.

d. Manganic Acid. $\mathrm{Mn\,O_3} = 51{\cdot}739$.

This acid has not been isolated. It is only known in combination with bases, especially potash, in which state it forms the chief ingredient of the mass called chameleon mineral, formed by igniting peroxide of manganese strongly with nitre, or still better by heating a mixture of peroxide, chlorate of potash and caustic potash. A dark green mass is formed, which is the chameleon mineral. The green colour is a property of manganic acid and all its salts. The peroxide obtains oxygen from the nitre or chlorate of potash, and the acid, when formed, combines with the potash. Water dissolves the manganate of potash, forming a splendid emerald-green solution, which very soon begins to change colour, and passes through bottle-green, blue, and purple, to a fine crimson red, hydrated peroxide of manganese being at the same time deposited. The red colour belongs to a salt of the next acid, permanganic acid (see below). The salts of manganic acid are decomposed if kept in solution, depositing hydrated peroxide.

e. Permanganic Acid. $Mn_2 O_7 = 111{\cdot}491$.

The salt of this acid with potash, permanganate of potash, is formed, when the chameleon mineral (see above) is dissolved in hot water. The green colour of the manganate changes to red, while hydrated peroxide separates. 3 eq. manganate of potash give rise to 1 eq. permanganate, 1 of peroxide, and 2 of free potash: $3(KO, Mn O_3) = Mn O_2 + (KO, Mn_2 O_7) + 2 KO$. When the red solution is sufficiently evaporated, it deposits small dark bronze-coloured crystals of permanganate of potash.

This salt is more permanent than the manganate; but when we attempt to isolate the acid, it is rapidly decomposed, yielding hydrated peroxide and oxygen gas, $Mn_2 O_7 = 2 Mn O_2 + O_3$.

The name of chameleon mineral was given to the compound above described from its singular changes of colour. Both the above acids possess and communicate to their salts very beautiful colours; but they cannot be used in dyeing, &c., because these acids are so easily decomposed, especially by the contact of organic matter. They ought to be filtered through asbestos when they require filtration.

f. Red Oxide of Manganese. $Mn_3 O_4 = 115{\cdot}152$.

This oxide occurs in nature, and may be obtained when any other oxide of manganese is strongly ignited in an open crucible. It is very permanent in composition: its colour is reddish-brown. It is not supposed to be an independent oxide of the metal, but rather a compound of two other oxides.

It may be either $MnO + Mn_2O_3$ or $MnO_2 + 2\,MnO$, and it is not easy to say which.

g. Varvicite. $Mn_4O_7 = 166{\cdot}8$.

This is another oxide, found native in Warwickshire, whence the name. It resembles the peroxide, but is really distinct. It is probably a compound of two others, $Mn_2O_3 + 2\,MnO_2$.

MANGANESE AND CHLORINE.

a. Protochloride of Manganese. $MnCl = 63{\cdot}15$.

This salt is best obtained by the following process:—The solution formed in the preparation of chlorine by means of peroxide of manganese and hydrochloric acid, which is generally a mixture of chloride of manganese and more or less perchloride of iron, is first rendered neutral by gently evaporating it to dryness. It is then redissolved, and a portion of it precipitated by carbonate of soda, which throws down a mixture of peroxide of iron and carbonate of manganese. $MnCl + Fe_2Cl_3$ acted on by $4\,(NaO, CO_2)$ yield $(MnO, CO_2) + Fe_2O_3 + 4\,NaCl + 3\,CO_2$. The precipitate is well washed, and then boiled with the rest of the solution, when the oxide of manganese in the precipitate acts on the perchloride of iron in the solution, producing chloride of manganese, which dissolves, and peroxide of iron, which separates. $3\,(MnO, CO_2) + Fe_2Cl_3 = 3\,MnCl + Fe_2O_3 + 3\,CO_2$. The filtered liquid is free from iron, if we have hit the proportion right; if not, a second operation with a smaller portion of the liquid will complete the purification. The pure solution is evaporated to dryness in a retort, and there fused. On cooling, the protochloride forms a pink crystalline mass. Iron is the ordinary impurity to be removed; but if other metals be present, they are to be got rid of by appropriate means. Thus, if cobalt and nickel are present, which they generally are in small quantity, the addition of hydrosulphuret of ammonia, as long as it causes a dark precipitate, or till it produces the pure flesh colour characteristic of manganese, will remove them. The chloride of manganese is used for preparing, by the action of an alkaline carbonate, pure carbonate of manganese, from which all other salts of manganese may be obtained.

b. Perchloride of Manganese. $Mn_2Cl_7 = 303{\cdot}19$.

This compound, which corresponds to the permanganic acid, is formed, according to Dumas and Wöhler, when permanganate of potash is heated along with common salt and sulphuric acid. $K O, Mn_2 O_7 + 7 Na Cl + 8 S O_3 = K O, S O_3 + 7 (Na O, S O_3) + Mn_2 Cl_7$. It is a greenish-brown volatile liquid, which is instantly decomposed by contact with moist air, forming a dense cloud of a pink colour. Here water is acted on, and the products are hydrochloric and permanganic acids. $Mn_2 Cl_7 + 7 H O = Mn_2 O_7 + 7 H Cl$.

e. Perfluoride of Manganese. $Mn_2 F_7 = 186{\cdot}46$.

When mineral chameleon (or better, permanganate of potash) is acted on by sulphuric acid and fluoride of calcium (fluor spar) with the aid of heat, a greenish-yellow gas or vapour is disengaged, which, with moist air, instantly becomes red. It acts powerfully on glass. Its composition seems to correspond to that of the preceding compound, and its production is to be explained in the same way, substituting fluoride of calcium for chloride of sodium. (Wöhler.)

d. Protosulphuret of Manganese. $Mn S = 43{\cdot}79$.

This compound is found native. It may be formed by passing a current of sulphuretted hydrogen over sulphate of manganese at a red-heat. The sulphuric acid of the sulphate is expelled, and the protoxide is acted on by the sulphuretted hydrogen. $Mn O + H S = Mn S + H O$. It is nearly black in colour, and dissolves readily in dilute hydrochloric and other acids, with disengagement of sulphuretted hydrogen. $Mn S + H Cl = Mn Cl + H S$. The flesh-coloured precipitate formed in salts of protoxide of manganese by hydrosulphuret of ammonia, or any other soluble sulphuret, is a hydrated protosulphuret of manganese, $Mn S, H O$.

27. IRON. $Fe = 28$.

This important and useful metal occurs very abundantly in nature. It is occasionally found in the uncombined state in masses, most probably of meteoric origin : but its most common form is that of oxide, frequently uncombined, frequently also combined with carbonic acid. It is found, likewise, abundantly as sulphuret. There is hardly a rock, a soil, or a mineral which does not contain some proportion, generally a small one, of oxide of iron : and the carbonate is a frequent ingredient in mineral waters, which are then termed chalybeate waters.

The chief ores of iron are—1. Clay iron stone, which is a more or less pure carbonate of protoxide, generally containing carbonates of lime and magnesia ; it accompanies coal beds both in England and in Scotland. 2. Red hematite, which is pure peroxide or sesquioxide of iron; and brown hematite, which is hydrated peroxide. 3. Black or magnetic oxide of iron.

From its ores iron is obtained by heating them in furnaces, in the upper part of which the ores are stratified with coal, lime, and sandstone. The carbon of the coal, at a red-heat, reduces the iron to the state of metal, while the sand and lime act as a flux, and form a liquid slag, through which the melted iron falls to the lower part of the furnace, where it is drawn off. The slag is drawn off separately after the iron, and on cooling is found to be a mixture of silicates of lime and magnesia with a little iron.

The iron thus obtained, which is called pig iron or cast iron, is not pure, containing some unreduced ore, or earthy matters, and a good deal of combined carbon. It is far more fusible than pure iron, but also far more brittle. To convert it into pure or malleable iron it is melted and exposed to a current of air, which gradually burns off the carbon. The mass is well stirred, and the other impurities rise to the surface as slag or dross. By degrees the metal becomes less fusible, and the heat must be increased, till at last, with the strongest heat, the metal continues solid. It is then well hammered while hot, by which it is still further purified, and rendered more dense. It is not yet absolutely pure, containing about $\frac{1}{2}$ per cent. of carbon and a trace of silicon. A very good test of the purity of iron is its ductility. Unless very pure, it cannot be drawn out into fine wire.

If perfectly pure iron is wanted, the filings of malleable iron should be fused with $\frac{1}{4}$ their weight of black oxide of iron, and some green glass to act as a flux. Or pure oxide of iron may be reduced to the metallic state by passing a current of hydrogen gas over it at a red-heat. The metal remains as a spongy mass.

Pure iron has a grey colour, and strong lustre when polished. It is very ductile, moderately malleable, and remarkably tenacious. It is hard at common temperatures, but at a red-heat it is so soft that it may be beaten into any form, and even admits of being welded; that is, two pieces of iron being heated red-hot, may be, by hammering, so incorporated into one, that no joining is perceptible. Its Sp. G. is 7·7. It is very infusible, requiring the very highest temperature of a wind furnace to melt it.

Iron is attracted by the magnet, and may itself be rendered permanently magnetic by various means.

The attraction of iron for oxygen is very powerful, and when exposed to air and moisture it rusts rapidly, forming oxide of iron. When heated to redness in air, iron is very quickly covered with a crust of black oxide, which scales off under the hammer. If heated to redness in oxygen, or to whiteness in the air, it burns with vivid scintillations. To secure the result in the air, the white hot metal must be exposed to a current of air from a bellows, or rapidly whirled round. Iron decomposes water rapidly at a red-heat.

IRON AND OXYGEN.

a. Protoxide of Iron. $Fe\,O = 36{\cdot}013$.

This oxide is a powerful base, almost unknown in a separate state, owing to its tendency to attract an additional quantity of oxygen. It combines with acids, forming salts, which have generally a pale bluish-green colour, although some are colourless. Several of these salts are of great importance in medicine and in the arts, particularly the sulphate of iron, or green vitriol.

The solutions of these salts give with alkalies, when no trace of peroxide is present, a bulky white precipitate of hydrated protoxide of iron, which soon becomes green, and lastly brown, being converted into peroxide by absorbing oxygen from the air. They give a similar precipitate, not more permanent, with carbonated alkalies ; which at first is hydrated carbonate of protoxide, but as oxygen is absorbed the carbonic acid is given off, peroxide of iron having no affinity for that acid. With ferrocyanide of potassium they give a pale blue, or rather a white precipitate, which gradually becomes dark blue, and with ferridcyanide of potassium (red prussiate) a deep blue precipitate of Prussian blue. These salts are not affected by sulphuretted hydrogen, sulphocyanide of potassium, meconic acid, or gallic acid. Hydrosulphuret of ammonia, and soluble sulphurets, produce a black precipitate of sulphuret of iron.

The salts of protoxide of iron, for the most part, attract oxygen from the air and from other bodies, passing into salts of the peroxide. Hence they act in some cases as deoxidising agents. Gold is completely reduced from its solutions by protosulphate of iron.

b. Sesquioxide of Iron. $Fe_2\,O_3 = 80{\cdot}039$.

Syn. *Peroxide of Iron.*—This oxide is found native, as red hematite and specular iron ore, and hydrated, as brown hematite. It may be prepared artificially by calcining pure, dried green vitriol, when the protoxide is oxidised at the expense of the sulphuric acid, and water, along with sulphuric and sulphurous acids, is expelled. $2\,(Fe\,O,\,H\,O,\,S\,O_3) = Fe_2\,O_3 + 2\cdot H\,O + S\,O_2 + S\,O_3$. A red powder is left, which is peroxide of iron, and in this form it is used for polishing plate, as jeweller's rouge, or colcothar of vitriol. Hydrated peroxide of iron is obtained by precipitating a solution of persulphate of iron, or perchloride of iron by an alkali, whether caustic or carbonated. When protosulphate of iron is precipitated by an alkaline carbonate, the precipitated protocarbonate, during the process of washing and drying, loses its carbonic acid, and attracts oxygen, becoming hydrated peroxide. This, when dry, is a brown powder, used in medicine under the erroneous name of carbonate of iron. In the moist state, it is the only known antidote to arsenious acid.

Peroxide of iron is not magnetic. It is a base, although not a powerful one, forming, with acids, salts which are either yellow, brown, or red. The solutions of such salts or persalts of iron, as they are called, are very easily recognised. They give, with caustic or carbonated alkalies, a brown precipitate of hydrated peroxide; with ferrocyanide of potassium a deep, Prussian blue; with ferridcyanide of potassium no precipitate; with sulphocyanide of potassium, or with meconic acid, a blood-red colour, and with tannic acid (or tannine) and gallic acid, a bluish-black colour (ink). Sulphuretted hydrogen causes a white precipitate of sulphur, while the peroxide is reduced to protoxide: hydrosulphuret of ammonia causes a black precipitate of sulphuret of iron. These tests are so delicate and so uniform, especially those of ferrocyanide of potassium, sulphocyanide of potassium and tannic acid, or infusion of galls, that it is always best in testing for iron, to convert any protoxide that may be present into peroxide, which is easily done by boiling the solution with a little nitric acid.

c. Magnetic oxide of Iron. $Fe_3O_4 = 116{\cdot}052$: and $Fe_4O_5 = 152{\cdot}065$.

This oxide is the native magnet, or loadstone, which is a heavy black mineral, strongly attracting iron filings, or steel. It is believed to be composed of protoxide and peroxide, and the native magnet is generally supposed to be $Fe_3\,O_4 = Fe\,O + Fe_2\,O_3$. There is reason, however, to believe, that another kind of magnetic oxide exists, which is $Fe_4\,O_5 = 2\,Fe\,O + Fe_2\,O_3$. At all events, both of these compounds may be formed artificially, and both are magnetic as well as permanent; not absorbing oxygen, or passing into peroxide.

To prepare the former, take 2 parts of green vitriol; dissolve it in water and convert it into persulphate by boiling with nitric acid; then mix the solution with the solution of 1 part of the unaltered green vitriol, and precipitate the hot liquid by ammonia. A green precipitate falls, which is to be washed and dried. The second magnetic oxide is prepared in the same way, only converting into persulphate 1 part of green vitriol instead of 2 parts. The precipitate is black, if made in the liquid while hot. It is evident that in the latter case the quantity of iron, in the forms of protoxide and of peroxide, will be equal; in the former, the quantity of iron in the peroxide will be double that in the protoxide, so as to yield the above formulæ. Magnetic oxide of iron is also formed when iron is heated red-hot, and hammered. The black scales which separate (smithy ashes) are magnetic. The same oxide is produced when the vapour of water is passed over iron at a red-heat, hydrogen being disengaged. It is used in medicine.

When black oxide of iron is dissolved in acids, both protoxide and peroxide are present. The latter may be precipitated by digestion with carbonate of lime, after which the former can be detected in solution.

IRON AND CHLORINE.

a. Protochloride of Iron. $Fe\,Cl = 63{\cdot}47$.

This compound is formed when dry hydrochloric acid gas is passed over iron heated to redness, hydrogen gas being disengaged. $Fe + H\,Cl = Fe\,Cl + H$. It appears as a white crystalline solid, volatile in a very high temperature. It dissolves readily in water, forming a pale-green solution, which yields on evaporation crystals of the same colour. These contain water of crystallisation. The characters of this solution, its colour, taste, and reactions, are so exactly those of a solution of a salt of protoxide, that there is good reason to conclude that the chloride, in dissolving, decomposes water, forming protoxide of iron and hydrochloric acid.

b. Perchloride of Iron. $Fe_2\,Cl_3 = 162{\cdot}35$.

SYN. *Sesquichloride of Iron: Permuriate of Iron.*—It is formed when chlorine gas is passed over iron heated to a temperature below redness, when it appears as red iridescent scales, volatile at a temperature little beyond 212°, and soluble in water, alcohol, and ether. A solution of the perchloride is easily obtained by dissolving peroxide of iron in hydrochloric acid : $Fe_2O_3 + 3HCl = Fe_2Cl_3 + 3HO$. When evaporated to the consistence of syrup, and cooled, it forms red crystals, which contain water of crystallisation. When heated, they are partly decomposed, peroxide being formed, and hydrochloric acid passing off, in consequence of the action between perchloride of iron and water. As perchloride of iron is a volcanic product, it is probably in this way that the crystals of peroxide, found in volcanic districts, have been formed. Perchloride of iron is much used in medicine.

IRON AND IODINE.

a. Protoiodide of Iron. $FeI = 154\cdot3$.

When iron filings and iodine, in atomic proportions, are brought in contact under water, they rapidly combine, with considerable heat, and the resulting iodide dissolves in the water. The whole is boiled with a slight excess of iron for a short time, and the pale-green filtered solution rapidly boiled down in a Florence flask, till on cooling it becomes solid. The solid mass of iodide is broken up, and kept in very closely-stopped bottles. It forms a dark grey crystalline mass, which is very soluble in water, and forms a pale-green solution; the solution, which is much used in medicine, attracts oxygen rapidly from the atmosphere, and is decomposed, iodine escaping, and peroxide being deposited. It is, therefore, necessary to prepare it extemporaneously, or to keep it in small tightly-corked bottles, with a portion of clear iron wire in each.

b. Periodide of Iron. $Fe_2I_3 = 434\cdot9$.

This compound is made by causing an excess of iodine to act on iron wire, and subliming the dry mass left after gently evaporating to dryness. It is a volatile, deliquescent body, of a red colour, soluble in water and alcohol.

The bromides of iron are analogous to the chlorides and iodides; and the fluorides correspond in composition, but are sparingly soluble in water.

IRON AND SULPHUR.

a. Protosulphuret of Iron. $FeS = 44\cdot12$.

This sulphuret is prepared by heating iron filings with sulphur in atomic proportions, when they combine with evolution of heat and light. Or a bar of iron may be heated to whiteness in a forge, and a stick of roll sulphur applied to the hot metal, which is instantly perforated, while the sulphuret falls to the ground in melted globules, having a yellowish colour and metallic lustre. Prepared by the first process, it is partly in crystalline grains, partly in the form of a black powder. It is used for procuring sulphuretted hydrogen gas, which is formed when the protosulphuret is dissolved in hydrochloric or sulphuric acid. $Fe\,S + H\,Cl = Fe\,Cl + H\,S$.

b. Sesquisulphuret of Iron. $Fe_2\,S_3 = 104{\cdot}36$.

It is formed by the action of hydrosulphuric acid (sulphuretted hydrogen) on peroxide of iron, at a heat not above 212°, as a yellowish-grey powder; or by adding perchloride of iron to an excess of hydrosulphuret of ammonia, as a black powder, rapidly oxidised by exposure to the air.

c. Bisulphuret of Iron. $Fe\,S_2 = 60{\cdot}24$.

SYN. *Iron Pyrites.*—This is a very abundant mineral, of a yellow colour and metallic lustre, crystallising in cubes or octahedrons. When heated in close vessels, it loses nearly half its sulphur, which may be collected, magnetic pyrites being left. Iron pyrites is often contaminated with arsenic, which accompanies the sulphur, and is found in the sulphuric acid made from it.

d. Magnetic Pyrites. $Fe_6\,S_7 = 280{\cdot}7$.

This also occurs in nature, and is attracted by the magnet. It dissolves in acids, yielding sulphuretted hydrogen and a residue of sulphur.

Arfwedson has formed two other sulphurets, the tetrasulphuret $Fe_4\,S$, and the disulphuret $Fe_2\,S$, which have no particular interest.

Diphosphuret of iron is an ingredient in some kinds of iron, and has the bad effect of rendering it cold short, that is, brittle at common temperatures.

IRON AND CARBON.

Iron forms with carbon two distinct compounds, the precise composition of which is unknown. These are cast iron and steel.

Cast iron is obtained in the process for extracting iron from its ores. It occurs in two forms, white and grey. Both fuse far more readily than pure iron. White cast-iron is very hard and brittle; it contains about 5 per cent. of carbon. Grey cast-iron is softer and tougher; it contains between 3 and 4 per cent. of carbon, in part uncombined.

Steel contains from 1·3 to 1·75 per cent. of carbon. It is less fusible than cast-iron, and is much harder, more elastic, and more sonorous than pure iron. It is made by cementation: that is, alternate layers of iron and charcoal are placed in a closed chamber and heated to redness for several days, during which time a gradual combination takes place.

28. ZINC. $Zn = 32{\cdot}3$.

This metal is found in considerable abundance. It occurs, as sulphuret, in zinc blende; and as carbonate of the oxide in calamine. To obtain the metal, the sulphuret is roasted in the air till the sulphur is burnt off and the zinc converted into oxide; or, what is preferable, the carbonate is heated till all the carbonic acid and water it contains are expelled, leaving oxide of zinc. The oxide is now mixed with charcoal and the mixture distilled in retorts, or in crucibles, closed at the top, but having a tube open at both ends fitted into the bottom, and reaching, within, nearly to the cover. The oxide is reduced by the action of the charcoal at a full red-heat, and the metal being volatile, distils over and is condensed in water.

Zinc has a bluish-white colour and bright lustre, and tarnishes slowly on exposure to the air. Its Sp. G. is about 7. It is brittle at ordinary temperatures; but, between 250° and 300°, it is both malleable and ductile, and may be rolled or hammered into sheets of considerable thinness. It melts at 773° (Daniell), and at a high red or white-heat sublimes or distils unchanged in close vessels. Heated strongly in air, it takes fire and burns with a beautiful white light, forming oxide of zinc.

ZINC AND OXYGEN.

Protoxide of Zinc. $ZnO = 40{\cdot}313$.

The oxide which is formed when zinc is burned in the air is the only compound of these elements. It may also be obtained by heating the carbonate to redness, or by precipitating the sulphate of zinc by a caustic alkali, in which latter case we obtain a bulky gelatinous hydrate of the oxide. Oxide of zinc is a fine white powder, insoluble in water, but very soluble in acids, which it neutralises, being a very powerful base, of the same class as magnesia.

Solutions of oxide of zinc are recognised by the following characters. Caustic alkalies produce a bulky white precipitate of hydrate, soluble in an excess of the alkali. The alkaline carbonates precipitate a bulky white carbonate of zinc, permanent when carbonate of soda or potash is employed, but soluble in excess of carbonate of ammonia. Sulphuretted hydrogen has no action if the solution be acid; but if it be quite neutral forms a white precipitate of hydrated sulphuret of zinc, which is best formed by hydrosulphuret of ammonia. Ferrocyanide of potassium also causes a white precipitate.

Chloride of Zinc. $Zn\,Cl = 67{\cdot}75$.

This compound is formed by the action of chlorine on zinc, or by dissolving zinc in hydrochloric acid, when hydrogen is evolved. $Zn + H\,Cl = Zn\,Cl + H$. The solution is evaporated to dryness and sublimed in a current of hydrochloric acid gas. It is white, semisolid, very fusible, volatile at a red-heat, and highly deliquescent. It was formerly called butter of zinc.

Iodide of Zinc. $Zn\,I = 158{\cdot}6$.

When iodine is acted on by excess of zinc under water, an energetic combination takes place, and a colourless solution is obtained which, in evaporation, leaves a deliquescent mass, very analogous to the chloride, and capable of being sublimed in crystals.

The bromide and fluoride of zinc are little known.

Sulphuret of Zinc. $Zn\,S = 48{\cdot}4$.

Sulphuret of zinc occurs native, under the name of zinc blende, in dodecahedral crystals, which are sometimes yellow, sometimes red, brown, or black. It may be formed by heating oxide of zinc with sulphur, or sulphate of zinc with charcoal, in a closed crucible. $Zn\,O, SO_3 + C_4 = 4\,CO + Zn\,S$.

29. CADMIUM. $Cd = 55{\cdot}8$

This metal occurs, in the form of carbonate, as an ingredient in various kinds of calamine or carbonate of zinc. It is also found in the form of sulphuret, as the rare mineral greenockite, and to the extent of 5 per cent. in some kinds of sulphuret of zinc. The metal is, in all its relations, very analogous to zinc, and is almost invariably found associated with it.

When an ore of zinc, containing cadmium, is treated as above described, to obtain the zinc, the first vapours that distil over, which are known as the brown blaze, contain the cadmium, and are separately collected. To purify it from zinc, it is dissolved in an acid, and the solution acted on by a piece of zinc in a platinum vessel. The cadmium is reduced, and adheres to the platinum, the zinc being dissolved in its place. When well washed, the cadmium may be dissolved off by nitric acid. Or the acid solution of both metals may be precipitated by sulphuretted hydrogen, which throws down cadmium and not zinc. The sulphuret of cadmium is then dissolved in nitric acid. From this solution alkalies throw down oxide of cadmium, which is reduced exactly like oxide of zinc.

Cadmium is in appearance similar to tin, but is harder and more tenacious. It is both malleable and ductile. Its Sp. G. is 8·6. It melts at about 450°, and boils at a temperature not a great deal higher than the boiling point of mercury. When strongly heated in the air, it burns, forming oxide. Like zinc, it forms only one oxide, chloride, sulphuret, &c.

Oxide of Cadmium. $Cd\,O = 63{\cdot}813$.

The oxide is best prepared by heating the carbonate to redness. It is an insoluble orange powder, which is a strong base, neutralising acids. Its salts are easily recognised by the following tests. Caustic alkalies cause a white, bulky precipitate of hydrated oxide, which dissolves in excess of ammonia. Sulphuretted hydrogen produces an orange precipitate of sulphuret of cadmium.

The chloride and iodide of cadmium are white fusible compounds.

The sulphuret of cadmium is an orange-yellow powder, soluble in nitric acid, and distinguished from yellow sulphuret of arsenic by being insoluble in caustic potash, and fixed in the fire.

30. TIN. $Sn = 57{\cdot}9$.

This important metal occurs in Cornwall and in Saxony, in the form of oxide, from which the metal is obtained by heating with charcoal.

Tin is a white metal, with a very high lustre, which is very little tarnished by exposure to the atmosphere. It is very malleable, yielding leaves (tinfoil) not thicker than $\frac{1}{1000}$ of an inch. It is soft, and when bent in the fingers makes a peculiar noise. Its Sp. G. is 7·2. It melts at 442°, and if heated to whiteness in air, it takes fire and burns with a white flame, forming peroxide of tin.

TIN AND OXYGEN.

a. Protoxide of Tin. $SnO=65{\cdot}913$.

This oxide is prepared by adding an alkaline carbonate to a solution of protochloride of tin, when a bulky white precipitate is formed of hydrated protoxide of tin. This is washed with warm water and dried at a heat not above 196°. The dry hydrate is now heated to redness in a current of carbonic acid gas, and the anhydrous protoxide is left.

Protoxide of tin is a dense black powder, which has so strong an attraction for oxygen, that if touched with a red-hot body, it takes fire and burns into peroxide. It dissolves in acids, forming salts which absorb oxygen with avidity, and reduce the oxides of silver, mercury, and platinum to the metallic state, if added to their solutions. With solutions of gold, salts of protoxide of tin produce a purple precipitate, the purple of Cassius; so that salts of gold and salts of protoxide of tin are mutually tests for each other. Salts of protoxide of tin give, with sulphuretted hydrogen, a black precipitate of protosulphuret of tin.

b. Sesquioxide of Tin. $Sn_2O_3=129{\cdot}839$.

When moist hydrated peroxide of iron is mixed with a neutral solution of protochloride of tin, an exchange takes place, and a bulky precipitate of a grey colour is formed, which is a hydrate of sesquioxide of tin. $Fe_2O_3+2\,SnCl=Sn_2O_3+2\,FeCl$. The sesquioxide is soluble in acids and in ammonia, the latter character distinguishing it from the protoxide. Its solution in hydrochloric acid forms, with chloride of gold, the purple of Cassius; and seems, indeed, better adapted for making it than the protoxide.

c. Peroxide of Tin. $SnO_2=73{\cdot}926$.

This oxide exists in two distinct modifications. 1. If made by the action of nitric acid on tin, which is very violent, it appears as a dense white opaque powder, which is a hydrate, insoluble in water or acids. 2. If prepared by adding potash to perchloride of tin, it forms a very bulky hydrate, readily soluble in acids and also in alkalies. It seems rather to possess the characters of a weak acid than of a base. It is recognised in its solution in acids, by forming with alkalies a bulky white hydrate, readily dissolved by excess of potash or soda, and by yielding, with sulphuretted hydrogen, a dirty yellow precipitate of bisulphuret of tin. When melted with glass, peroxide of tin renders it opaque, forming a white enamel.

TIN AND CHLORINE.

a. Protochloride of Tin. $Sn\,Cl = 93{\cdot}37$.

This chloride is formed when chlorine gas is passed over metallic tin moderately heated, when hydrogen is given off. When dry it is a grey solid, fusible below redness. Tin dissolves in hydrochloric acid, and the concentrated solution deposits acicular crystals, which are a hydrated chloride, $Sn\,Cl + 3\,H\,O$. When heated, they give off water and hydrochloric acid, while protoxide is left: $Sn\,Cl + 3\,H\,O = Sn\,O + H\,Cl + 2\,H\,O$. The addition of a large quantity of water decomposes these crystals, causing the formation of an insoluble white powder, which is a compound of oxide and chloride with water. The solution of protochloride of tin, made by digesting an excess of tin in hydrochloric acid as long as hydrogen is given off, is much used as a deoxidising agent. It is apparently resolved into bichloride and metal, $2\,Sn\,Cl = Sn\,Cl_2 + Sn$; and the latter, probably, is the true agent in deoxidising. It is also used for making the purple of Cassius.

b. Perchloride of Tin. $Sn\,Cl_2 = 128{\cdot}74$.

When protochloride of tin is heated in excess of chlorine gas, or when 8 parts of tin powder are distilled with 24 of bichloride of mercury, a volatile fuming liquid is obtained, formerly known as the fuming liquor of Libavius, which is bichloride of tin. It is obtained in solution by dissolving tin in nitro-hydrochloric acid of moderate strength, adding small portions of tin at a time; also by forming a solution of protochloride, and passing chlorine through it, or heating it gently with a little nitric acid. It is much used in dyeing as a mordant.

The protoiodide of tin is a brownish-red fusible solid, dissolving in water; the periodide forms silky yellow crystals.

TIN AND SULPHUR.

a. Protosulphuret of Tin. $Sn\,S = 74$.

This compound is formed by pouring melted tin on its own weight of sulphur, and stirring well. The mass is then powdered, mixed with more sulphur, and thrown by degrees into a red-hot crucible, by which means the whole of the tin is sulphurised. It forms a bluish-black brittle solid, having metallic lustre. It is also formed when sulphuretted hydrogen acts on solutions of protoxide or protochloride of tin.

b. Persulphuret of Tin. $SnS_2 = 90{\cdot}1$.

This sulphuret, formerly called *aurum musivum*, is prepared by heating to low redness, in a retort, a mixture of 2 parts peroxide of tin, 2 of sulphur, and 1 of sal-ammoniac. The sulphuret is left in the form of golden-yellow scales, having a metallic lustre. It is soluble in potash. It is also formed as a dirty-yellow bulky hydrate by the action of sulphuretted hydrogen on solutions of peroxide or perchloride of tin.

31. COBALT. $Co = 29{\cdot}5$.

This metal occurs pretty abundantly, generally combined with arsenic, and associated with nickel and iron. A trace of it is always found in meteoric iron. To obtain the metal from the arseniuret, the ore, finely powdered, is gradually added to 3 parts of bisulphate of potash, melted in a moderate heat, and gradually increasing the fire, till no more white fumes appear. The mass, when cold, is powdered and boiled with water as long as anything is dissolved. The solution is free from arsenic, and contains sulphate of protoxide of cobalt. It is precipitated by carbonate of soda, and the washed precipitate acted on by oxalic acid, which forms an insoluble pink powder of oxalate of protoxide of cobalt. Should iron be present, it forms a soluble compound with the oxalic acid, provided it has been brought into the state of peroxide by boiling the solution with a little nitric acid before precipitating with carbonate of soda. The only impurity now likely to be present is nickel, and to separate this, the oxalate is dissolved in an excess of ammonia, and the solution exposed to the air in a deep glass vessel. As the ammonia evaporates, the nickel is deposited (if present) in the form of a pale-green insoluble double oxalate of nickel and ammonia, while the cobalt remains dissolved, forming a port-wine-coloured solution. This being digested with excess of potash, yields a dark brown precipitate of pure peroxide of cobalt. This is again dissolved in hydrochloric acid, the solution precipitated by caustic potash or carbonate of soda, and the precipitate converted into oxalate, which is now quite pure; and the oxalate being heated to whiteness in a closed crucible, with a small aperture for escape of gas, leaves a button of pure metallic cobalt. The oxalate of cobalt, CoO, C_2O_3, is resolved by the heat into carbonic acid and metal, $CoO, C_2O_3 = Co + 2\,CO_2$.

Cobalt is a metal of a reddish grey colour, rather brittle and very infusible. Its Sp. G. is 7·8. It is attracted by the magnet. At a red-heat it decomposes water, hydrogen being disengaged.

COBALT AND OXYOEN.

a. Protoxide of Cobalt. $Co\,O = 37{\cdot}513$.

Obtained by calcining carbonate of cobalt in close vessels, as an ash-grey powder. It is a strong base, and forms, with acids, salts which are either pink or blue. Zaffre and smalt, which are so much used for painting blue on porcelain, and by the paper-makers to correct the yellow tinge of their paper, are silicates of this oxide. The solutions of its salts are precipitated by caustic alkalies, which form a blue hydrate, gradually changing to green, soluble in excess of ammonia. Carbonates produce a lilac-coloured precipitate of carbonate of cobalt. Sulphuretted hydrogen produces no change: hydrosulphuret of ammonia produces a black sulphuret.

When this oxide, or the peroxide of cobalt, are heated in the air, they both yield a black oxide, which corresponds to the red oxide of manganese, its formula being $Co_3\,O_4 = Co\,O + Co_2\,O_3$. The green hydrate, formed when hydrate of the protoxide is exposed to the air, is a hydrate of this oxide.

b. Peroxide of Cobalt. $Co_2\,O_3 = 83{\cdot}039$.

Syn. *Sesquioxide of Cobalt.*—When bleaching liquor (hypochlorite of lime) is added to solutions of protoxide of cobalt, or when chlorine is passed through hydrated protoxide suspended in water, a black powder is formed, which is hydrated peroxide. 3 eq. protoxide, and 1 eq. chlorine, yield 1 eq. protochloride and 1 eq. peroxide. $3\,Co\,O + Cl = Co_2\,O_3 + Co\,Cl$.

Peroxide of cobalt is, like peroxide of manganese, an indifferent or neutral oxide, for it does not combine with acids; and when dissolved in hydrochloric acid, it forms protochloride, chlorine being disengaged.

Chloride of Cobalt. $Co\,Cl = 64{\cdot}95$.

Obtained by dissolving cobalt, or any of its oxides, in hydrochloric acid. The solution is pink, and on evaporation yields beautiful red crystals of hydrated chloride, or possibly hydrochlorate of the oxide. When dried by heat, the chloride is of a deep blue, but is instantly rendered pink by the contact of water. The crystals are either $CoCl, HO$, or CoO, HCl. When traces are made on paper with a dilute solution of chloride of cobalt, they are invisible when dry; but, when warmed, assume a decided blue colour, which disappears again on cooling, as they again absorb moisture from the air. This is the most beautiful of the sympathetic inks. If iron or nickel be present, the traces appear green instead of blue.

The sulphurets of cobalt are not of much interest. The protosulphuret, CoS, is formed when hydrosulphuret of ammonia acts on salts of protoxide of cobalt as a black precipitate. According to Wöhler, sulphuret of cobalt is easily obtained by fusing the arseniuret of cobalt with 3 parts of pearlash and 3 parts of sulphur. The arsenic forms a soluble compound, and this is removed by water, leaving sulphuret of cobalt as a black powder. This may be dissolved in nitric acid, and the cobalt purified from iron and nickel, as above described. This process for extracting cobalt from its ores would seem to be the best of all.

The compounds of cobalt, when fused with glass, give to it a beautiful blue colour, and their use in painting the blue patterns on china is well known. The finest cobalt-blue for painting is made by heating a mixture of 15 parts of alumina with 2 of phosphate of cobalt to redness.

32. NICKEL. $Ni=29{\cdot}5$.

This metal is rather rare; it occurs, like cobalt, chiefly in combination with arsenic, and associated with iron and cobalt. A very good method of extracting it from the arseniuret, or speiss, as it is called, is that of Wöhler, which is, to fuse the speiss with 3 parts of pearlash and 3 parts of sulphur. The arsenic forms, with the sulphur and potash, a soluble compound, and the nickel forms with the sulphur an insoluble sulphuret. This is well washed with water, and dissolved in nitric acid; and the solution, after any lead, copper, or bismuth that may be present, have been precipitated by a current of sulphuretted hydrogen, is precipitated by caustic or carbonated potash or soda. The washed precipitate is now acted on by an excess of oxalic acid, which forms, with the peroxide of iron that is generally present, a soluble, and with the oxide of nickel an insoluble oxalate, which of course includes any cobalt that the ore may have contained. The oxalate is now dissolved in an excess of ammonia, and the solution exposed to the air. As the ammonia escapes, the nickel is deposited as an insoluble double oxalate, while the cobalt remains dissolved as a soluble double oxalate, of the metallic oxide with ammonia. The nickel salt, being ignited, leaves oxide, which may be reduced by heating with charcoal, or dissolved in acid, and again converted into oxalate, which this time is free from cobalt, and appears as a pale apple-green powder. The oxalate of nickel, being well washed, dried, and ignited in a closed crucible, with an aperture for the escape of gas, leaves metallic nickel, which, if the heat be very intense, is fused into a button.

Wöhler gives another process, which is said to be preferable to the above. It consists in projecting the finely powdered ore along with 2 parts of nitre and one of carbonate of potash, by degrees, into a red-hot crucible, and finally raising the heat for a good while. The arsenic is oxidised, yielding arsénic acid, which unites with the potash, while the nickel is also oxidised, and forms oxide of nickel, which is left undissolved when the mass is lixiviated with water. This oxide is pure, except from cobalt and iron, which must be separated as above. When these metals are not present, the oxide may be at once reduced by heating with charcoal, and yields pure nickel.

Nickel is nearly silver-white, but has a tinge of grey. It has a high lustre, is hard, and malleable. Its Sp. G. is 8·9. It is very infusible, and decidedly magnetic. It decomposes water at a red heat. Magnetic needles may be made of it, which do not rust. It is now much used in the manufacture of German silver or argentan, which is an alloy of copper, zinc, and nickel. The better qualities contain more nickel than the inferior kinds.

NICKEL AND OXYGEN.

Protoxide of Nickel. $NiO = 37{\cdot}513$.

Its preparation is given above, in Wöhler's second process for metallic nickel. It is a greenish-grey powder, which is a base, and forms, with acid, salts which are all green of different shades. Solutions of these salts give pale apple-green precipitates of hydrate and carbonate, with caustic and carbonated potash and soda. Ammonia causes a slight precipitate, which is instantly redissolved by an excess, forming a violet-blue solution. Salts of nickel are not precipitated, in acid solutions, by sulphuretted hydrogen, but hydrosulphuret of ammonia causes a black precipitate of sulphuret of nickel.

b. Peroxide of Nickel. $Ni_2O_3 = 83{\cdot}039$.

Syn. *Sesquioxide of Nickel*—May be formed by passing chlorine through water in which the hydrated protoxide is suspended. It is an indifferent oxide or superoxide, analogous to sesquioxide of cobalt. It is a black powder.

Chloride of Nickel. $NiCl = 64{\cdot}95$.

Analogous to chloride of cobalt. Its solution is emerald-green, and yields crystals of the same colour; but when entirely deprived of water, it is yellow. At a low red heat it sublimes and condenses in brilliant gold-yellow scales.

Protosulphuret of Nickel. $NiS = 45{\cdot}6$.

Analogous to protosulphuret of cobalt, and formed in the same way. Sulphur and nickel unite when heated together, with disengagement of heat and light, forming a greyish-yellow metallic mass. The precipitated sulphuret is black. Sulphuret of nickel is found native in fine crystals of a pale brass colour, as the Haarkies of the Germans.

ORDER 2.—METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

33. ARSENIC. $As = 37{\cdot}7$.

This metal is occasionally found native, but it is chiefly met with in combination with cobalt, nickel, and iron. When the arseniurets of these metals are heated to redness in a current of air, a great part of the arsenic, being volatile, rises in vapour, and is deposited in the cold part of the chimney in the form of white oxide of arsenic or arsenious acid, the well-known white arsenic of commerce. This substance is mixed with charcoal or black flux (a mixture of charcoal with carbonate of potash), and the mixture introduced into a medicine phial, filling it about one-third. The phial is then placed in sand, the sand reaching as high as the mixture, and gradually heated to low redness. The metal sublimes and condenses in the upper part of the phial, which, when cold, may be cut off.

Arsenic is a very brittle metal, of a whitish-grey colour, and very high lustre. Its Sp. G. is 5·80. When heated to 356°, it sublimes without previously melting, its melting point being higher than its boiling point under the usual pressure. Its vapour has a strong alliaceous smell, a property which is characteristic of arsenic, no other metal possessing it. It sometimes rapidly tarnishes on exposure to the air, becoming nearly black; and when sublimed in a current of air it is oxidised, being converted into arsenious acid. The rapid tarnishing of arsenic is probably owing to the presence of a little potassium, derived from black flux; for the native metal, when sublimed, does not tarnish.

ARSENIC AND OXYGEN.

a. Arsenious Acid. $As_2\ O_3=99{\cdot}439$.

The formation of this substance, when arsenic is sublimed in a current of air, has been mentioned. It occurs, when newly sublimed, as a hard brittle glass, which, when kept, slowly becomes opaque and crystalline, the change often taking years to reach the centre of a small lump of the glass. The Sp. G. of arsénic acid is 3·7. At 380° it sublimes, yielding inodorous vapours, which condense in octohedral crystals, when the sublimation is slowly conducted in a glass tube.

It has little taste, which renders it the more dangerous as a poison: as, when taken by mistake, there is no warning, as in the case of many other poisons. It is sparingly soluble in water, but the crystalline variety is more soluble than the glassy; 100 parts of hot water dissolving 11·5 of the former, and only 9·7 of the latter.

Arsenious acid, whether in the solid form or in that of solution, is a most virulent poison, and is, unfortunately, so accessible as to be often used for criminal purposes. Its detection, therefore, is a matter of the utmost importance; and innumerable tests, more or less effectual, have been proposed. These, however, may with advantage be reduced to a very small number; which again are best divided into—1. Those tests which apply to pure arsenious acid, or its salts; and, 2. Those which apply to mixtures, such as are likely to occur in medico-legal investigations.

1. Pure arsenious acid is easily recognised, as a heavy white powder, volatile without smell, sparingly soluble in water, and, when heated with charcoal, black flux, formiate of soda, or cyanide of potassium, yielding a volatile crust of metallic arsenic, the vapours of which have the odour of garlic.

The solution gives, with lime-water in excess, an insoluble white precipitate of arsenite of lime; with ammoniaco-nitrate of silver, a yellow precipitate of arsenite of silver; with ammoniaco sulphate of copper, a grass-green precipitate of arsenite of copper; and with sulphuretted hydrogen, acetic or hydrochloric acid being first added to the solution, an orange-yellow precipitate of sesquisulphuret of arsenic. When to the solution of arsenious acid, or of any of its salts, sulphuric acid is added, and a portion of pure zinc introduced into the acid liquid, the hydrogen disengaged by the action of the zinc on the acid is found to be mixed with a portion of arseniuretted hydrogen gas, the presence of which gives it an alliaceous smell, and causes it to burn with a pale blue flame. If a piece of cold glass or porcelain be held in contact with this flame, a black stain or crust of metallic arsenic is deposited on it, and this crust may easily be recognised by its volatility, and the other characters of arsenic. (Marsh.) If the hydrogen gas, containing arseniuretted hydrogen, instead of being burned at the end of the tube, be slowly passed through a long narrow tube of hard glass, part of which is heated to redness, the arseniuretted hydrogen is decomposed at the red-hot part of the tube, and the arsenic deposited as a bright metallic crust a little beyond the hot part.

2. When, however, arsenious acid occurs in mixtures containing much organic matter, such as, for example, are found in the stomach or intestines of those poisoned with arsenic, or in the matters vomited before death, a method must be adopted which removes all organic matters, and permits the operator to test for arsenic with security. The following method, lately proposed by Fresenius and Von Babo, is perhaps the best :—

a. Two-thirds of the suspected mixture, or contents of a stomach, all solid parts being cut small, are introduced into a large porcelain capsule (the remainder being kept in case of accidents), and mixed with a moderate quantity of pure hydrochloric acid, and as much water as gives to the whole the consistence of a thin gruel, which is heated in the vapour bath, and chlorate of potash added at intervals of five minutes in portions of 20 or 30 grains to the hot liquid, until the whole has become clear yellow, perfectly homogeneous and fluid. At this point, about 2 drachms more of chlorate are added, and the vessel removed from the vapour bath. When quite cold it is strained through linen, or filtered, and the residue on the filter well washed with hot water. The whole liquid is now evaporated on the water bath to the bulk of about one pound, and the acid residue, which is generally now brownish in colour, mixed with as much of a saturated solution of sulphurous acid as gives a permanent smell of that acid. It is then heated until the excess of sulphurous acid is entirely expelled.

In this first stage of the process the arsenious acid is dissolved, the organic matter destroyed in a great measure by the chlorate of potash and hydrochloric acid, and the arsenic, which had thereby been converted into *arsénic* acid, reduced by the sulphurous acid to the state of arsenious acid. The destruction of the organic matter renders the filtration rapid and easy.

b. The acid liquid is now exposed for twelve hours to a current of sulphuretted hydrogen gas, the gas tube is washed with a little ammonia, which is added to the mass of liquid, and the whole allowed to stand, covered with paper, in a warm place, until the smell of sulphuretted hydrogen disappears. The precipitate which has formed, and which contains sulphuret of arsenic along with some organic matter, and possibly other metallic sulphurets, is collected on a small filter and well washed.

Here the arsenious acid is converted into sesquisulphuret of arsenic by the sulphuretted hydrogen. $As_2\,O_3 + 3\,HS = As_2\,S_3 + 3\,H\,O$.

c. The filter with the precipitate is dried in the vapour bath, moistened with fuming nitric acid, and the mass dried up in the water bath. Pure oil of vitriol is now added, so as to moisten the dry mass uniformly, the mixture is heated for two or three hours in the vapour bath, and, finally, dried on the sand bath at a heat not exceeding 290°, till the charred mass assumes a brittle consistence. It is then heated in the vapour bath with from ten to twenty parts of distilled water, filtered, and the charcoal perfectly washed with hot distilled water. The whole filtered liquid is now mixed with hydrochloric acid and again precipitated by sulphuretted hydrogen, exactly as before. The precipitate is collected on a very small filter, well washed, and dissolved on the filter by ammonia, with which the filter is well washed. The ammoniacal solution of sulphuret of arsenic is evaporated to dryness in a small porcelain vessel, and the residue may be weighed if required.

In this stage the remaining organic matter is entirely destroyed, and the arsenic obtained in the form of pure sesquisulphuret.

d. For obtaining the metallic arsenic from this sulphuret, or reducing the sulphuret, which is the decisive proof, the following apparatus is employed (see cut, fig. I). A is a well sized flask for generating carbonic acid gas, half filled with water

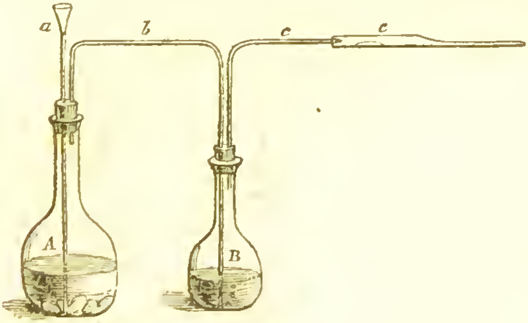


FIG. I.

and fragments of marble. Through one aperture in the cork passes the funnel tube *a*, reaching nearly to the bottom; through the other passes a tube *b*, which conducts the gas into the smaller flask B, in which it is washed and dried by passing through oil of vitriol. The tube *c* carries the gas into the reduction tube C, which is represented in fig. II., a little less than half the real size.

When the whole is fitted and arranged, a portion of the dried sulphuret (reserving part for other experiments, or in case of accident), is mixed in a warm agate mortar with about twelve parts of a mixture of three parts of dried carbonate of soda and one part of cyanide of potassium. The mixed powder is carefully introduced, by means of a half cylinder of card, into the reduction tube, which is then turned on its axis, so as to allow the powder to lie on the part *a f*, fig. II. of the reduction tube. The card is then removed. The reduction tube is now attached to the gas apparatus, and hydrochloric acid poured into the flask A, through the funnel, so as to cause a disengagement of carbonic acid gas, which fills the whole apparatus. The tube is then gently warmed through its whole length until all traces of moisture have disappeared, and when the current of gas has become so slow that the bubbles follow each other at an interval of about a second, the part *b* of the reduction tube (fig. II.), is heated to redness by a spirit lamp. This being done, the powder is now heated by another spirit lamp from *a* towards *f*, gradually, till all the arsenic is expelled.

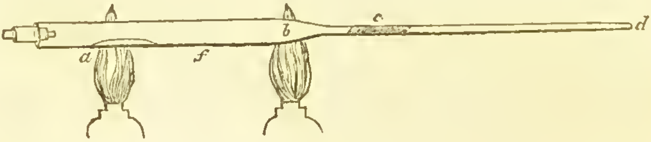


FIG. II.

The reduced arsenic is deposited as a bright metallic ring at *c*, fig. II., a mere trace only escaping at *d*. The second lamp is then brought towards *b*, in order to collect any trace of arsenic in the wide part of the tube, and the point *d* being closed by melting it, and the tube detached, the arsenic is driven into as small a space as possible by heating from *d* towards *c*. The tube is now cut across at *f*, corked, sealed, and preserved as evidence. If the above process be followed exactly, the result is a ring of astonishing purity and brilliancy. The use of the carbonic acid is to prevent oxidation by the air, which, as well as moisture, if admitted, would very much interfere with the result.

This is not the place to notice the very numerous methods which have been proposed for the detection of arsenic in mixed fluids. It is enough to say that none of them is preferable to the above, if indeed any are equal to it, in point of facility, delicacy, and security. The process of Marsh, by hydrogen gas, as above described, is indeed very delicate, but it is rendered less secure by the fact that antimony, if present, gives somewhat similar appearances. In the method of Fresenius and Von Babo, antimony, if present, remains in the residue of the powder heated in the reduction tube, where it may be found, chiefly in the metallic state, and partly in a soluble combination.

The only known antidote to arsenious acid is the hydrated peroxide of iron, the ferrugo of the Edin. Pharmacopœia, which should be given in the moist state mixed with water. When made for this purpose, the precipitated oxide should never be dried, but kept under water; as when once dried, it is far less efficacious. It acts by combining with the arsenious acid, forming a compound which is quite insoluble and inert, and is a basic arsenite of sesquioxide of iron, $Fe_2 O_3, As_2 O_3$.

b. Arsénic Acid. $As_2 O_5 = 115{\cdot}465$.

This acid is found in nature combined with oxides of calcium, lead, copper, iron, cobalt, and nickel. It is easily prepared by dissolving arsenious acid in nitric acid, with a little hydrochloric acid, and evaporating to a syrup, which is heated gently till all nitric acid is expelled. The residue is hydrated arsénic acid, $As_2 O_5, 3\,HO$, or $As_2 O_8, H_3$. It is a very acid, poisonous substance, remarkable chiefly for its analogy with common or tribasic phosphoric acid. This analogy is so great, that for every tribasic phosphate, there is a corresponding arseniate: and this is not all, for the external properties of these salts are so exactly similar, that, except by analysis, or characteristic tests, we cannot tell whether arsénic, or phosphoric acid, be present. Not only are the native phosphates of copper, lead, and iron, exactly like the arseniates in colour, crystalline form, and constitution, but the phosphates are seldom found unmixed with arseniates.

The complete isomorphism of arsénic and tribasic phosphoric acids, in their salts, is one of the finest examples of isomorphism depending on similarity of constitution. Like the tribasic phosphates, the arseniates occur in 3 forms.

$$1\text{st, } As_2O_5, 3\,MO : 2\text{nd, } As_2O_5 \left\{ \begin{matrix} 2\,MO \\ HO \end{matrix} \right. : 3\text{rd, } As_2O_5 \left\{ \begin{matrix} MO \\ 2HO \end{matrix} \right. :$$

and the crystalline form in all yet examined is the same as that of the corresponding phosphates. Thus the arseniate of soda, with 2 eqs. soda, and 1 eq. water, is not to be distinguished, in external aspects, from the common phosphate of soda. The formulæ are—

$$P_2O_5 \left\{ \begin{matrix} 2\,NaO \\ HO \end{matrix} \right. + 24\text{ aq : and } As_2O_5 \left\{ \begin{matrix} 2\,NaO \\ HO \end{matrix} \right. + 24\text{ aq.}$$

It is highly probable that phosphorus and arsenic are themselves entirely isomorphous as elements: and in one particular they are alike, besides the analogy of their compounds; namely, the alliaceous odour of their vapour.

The salts of arsénic acid give with nitrate of silver a brick-red precipitate of tribasic arseniate of silver; $As_2O_5, 3\,AgO$: and with hydrochloric acid and sulphuretted hydrogen, a pale yellow precipitate of persulphuret of arsenic, As_2S_5.

No modifications of arsénic acid, analogous to bibasic and monobasic phosphoric acids, are yet known.

ARSENIC AND CHLORINE.

Sesquichloride of Arsenic. $As_2Cl_3 = 181{\cdot}66$.

Prepared by distilling 6 parts of bichloride of mercury with 1 part of metallic arsenic, $3\,HgCl_2 + As_2 = 3\,HgCl + As_2Cl_3$. It is a colourless, volatile, fuming liquid, which is resolved, by the action of water, into hydrochloric and arsenious acids. $As_2Cl_3 + 3\,HO = As_2O_3 + 3\,HCl$.

ARSENIC AND IODINE.

Periodide of Arsenic. $As_2I_5 = 706{\cdot}9$.

When arsenic and iodine are gently heated together they combine, and form a red solid compound, which by the action of water yields arsénic and hydriodic acids. $As_2I_5 + 5\,HO = As_2O_5 + 5\,HI$.

ARSENIC AND BROMINE.

Sesquibromide of Arsenic. $As_2Br_3 = 313{\cdot}6$.

Arsenic and bromine when brought in contact, instantly combine, with vivid combustion. The compound is a solid, melting at about 70°, and boiling at 430°. It is transparent, and slightly yellow, and occasionally forms long prismatic crystals. With water, it yields arsenious and hydrobromic acids.

ARSENIC AND HYDROGEN.

When an alloy of arsenic and potassium is made to act on water, there is formed a brown solid body, which is said to be a protohyduret of arsenic, As H = 38·7.

When arsenic is melted with an equal weight of zinc, an alloy is formed, which, when acted on by strong hydrochloric acid, yields a gas which is colourless, has a strong garlic odour, burns with a blue flame, and is distinguished from all other gases by being totally absorbed, when pure, by a saturated solution of sulphate of copper. It is frightfully poisonous when respired even in very small proportion along with common air, and the incautious experimenting with it has proved fatal to more than one chemist. It acts on many metallic solutions, forming insoluble arseniurets. When heated to redness it is decomposed, arsenic being deposited, and hydrogen, equal to one and a half time the bulk of the gas, being separated. This gas is formed when hydrogen is generated in a liquid containing arsenious acid dissolved, and mixes with the hydrogen; and when the mixture is heated red-hot in passing through a tube, or burned, a cold plate being held in the flame, arsenic is deposited. This is the principle on which Marsh's process for detecting arsenious acid is founded.

ARSENIC AND SULPHUR.

a. Protosulphuret of Arsenic. As S = 53·8.

Formed by melting arsenious acid with half its weight of sulphur. It is a red translucent solid, which may be sublimed in close vessels. It occurs in the mineral kingdom as realgar.

b. Sesquisulphuret of Arsenic. $As_2 S_3 = 123{\cdot}7$.

Prepared by melting together equal weights of arsenious acid and sulphur, or by passing a current of sulphuretted hydrogen through a solution of arsenious acid. It has an orange-yellow colour, is fusible, and may be sublimed in close vessels. It is very soluble in caustic alkalies, yielding colourless solutions. It occurs in the mineral kingdom as auripigmentum, or orpiment, and is an ingredient in king's-yellow. It may be used for dyeing silk, woollens, or cottons yellow, by soaking them in a solution of orpiment in ammonia, and then suspending them in a warm chamber. The ammonia evaporates, and the orpiment remains firmly fixed in the cloth. This sulphuret is the form in which arsenic is best separated from mixed liquids in medico-legal investigations.

c. Persulphuret of Arsenic. $As_2 S_5 = 156$.

Formed by the action of sulphuretted hydrogen on arsénic acid, or on arseniates acidulated by acetic acid. It is of a paler yellow than orpiment, is soluble in alkalies, fusible, and in close vessels volatile without change.

34. CHROMIUM. $Cr = 28$.

Occurs in nature, in union with oxygen, as chromic acid in chromate of lead, and as oxide of chromium in chrome iron ore, from which latter all the compounds of chromium are obtained. The metal is very infusible, and has probably never been completely melted. It is obtained with difficulty in hard coherent masses of an iron-grey colour, by heating the oxide to the highest temperature of a wind furnace for some hours in a crucible lined with charcoal. In this state it is hardly at all acted on by the strongest acids, but is oxidised by fusion with nitre, yielding chromic acid.

CHROMIUM AND OXYGEN.

a. Sesquioxide of Chromium. $Cr_2 O_3 = 80{\cdot}039$.

This oxide may be obtained by heating to redness the bichromate of potash, $KO, 2\,Cr\,O_3$; when neutral chromate, $KO, Cr\,O_3$, is formed, sesquioxide is produced, $Cr_2\,O_3$, and oxygen is disengaged, $2\,(KO,\ 2\,Cr\,O_3) = 2\ (KO,\ Cr\,O_3) + Cr_2\,O_3 + O_3$. The neutral chromate is dissolved out by water and the oxide is obtained as a crystalline green powder; or it may be prepared by heating a mixture of bichromate with carbonate of soda and sal ammoniac to redness. The hydrate is obtained by heating solution of bichromate with hydrochloric acid and alcohol or sugar till the liquid becomes of a pure green, and adding ammonia, which precipitates the hydrate as a pale bluish-green bulky powder.

Sesquioxide of chromium is isomorphous with sesquioxide of iron and alumina, and has been obtained in crystals exactly resembling specular iron ore. It is a weak base, and may be substituted for alumina or peroxide of iron in their salts, without altering the form. All its salts are green or blue, and most of them are red by transmitted candle-light. Oxide of chromium appears to exist in its salts in two modifications, in one of which the solutions are pure green, in the other of a mixed tint of red and green. The oxide may be used for painting a beautiful green on china, and for giving glass a green colour, or as a paint, being very permanent.

b. Chromic Acid. $Cr\,O_3 = 52{\cdot}039$.

Prepared by adding 1 vol. of a cold saturated solution of bichromate of potash to 1½ vol. of pure oil of vitriol, and allowing the mixture to cool in a covered capsule, or in a flask, when it deposits beautiful deep-red needles of chromic acid. The liquid being drained off, these are laid on a porous brick to dry, covered with a bell jar. They must be preserved in very tightly-stoppered bottles, as they are highly deliquescent.

Chromic acid is a strong acid, isomorphous with sulphuric, selenic, and manganic acids. Its salts are yellow, orange or red, and distinguished by the beauty and permanence of their colours. The acid itself is a powerful oxidising agent, yielding half its oxygen readily to oxidisable bodies, and being reduced to sesquioxide: $2\,Cr\,O_3 = Cr_2\,O_3 + O_3$. Thus it instantly sets fire to alcohol when thrown into that fluid; and a mixture of bichromate of potash and sulphuric acid is much used as a means of oxidising organic products, and yielding new compounds. Chromic acid and oxide of chromium are both easily recognised in solutions by their colour, and the acid especially by its ready convertibility into the oxide by deoxidising agents.

According to Barreswill there exists a perchromic acid, $Cr_2\,O_7$, corresponding to permanganic acid. It is formed by the action of peroxide of hydrogen on chromic acid, and has a fine deep-blue colour. It is almost immediately resolved, however, into chromic acid and oxygen.

CHROMIUM AND CHLORINE.

a. Sesquichloride of Chromium. $Cr_2\,Cl_3 = 162{\cdot}26$.

Prepared by passing chlorine over a mixture of sesquioxide of chromium and charcoal heated to redness. It collects in the cold part of the tube as a crystalline peach-blossom-coloured sublimate, which dissolves in water, forming a green solution, which probably contains hydrochloric acid and sesquioxide, $Cr_2Cl_3 + 3\,H\,O = Cr_2\,O_3 + 3\,H\,Cl$. The sesquichloride exists in another modification as a pink insoluble powder.

b. Oxychloride of Chromium. $Cr\left\{\begin{matrix}O_2\\ Cl\end{matrix}\right.$, or $Cr\,Cl_3 + 2\,Cr\,O_3$.

This compound is formed when neutral chromate of potash, common salt, and oil of vitriol are heated together, $(K\,O,\,Cr\,O_3) + Na\,Cl + 2\,S\,O_3 = (K\,O,\,S\,O_3) + (Na\,O,\,S\,O_3) + Cr\,O_2\,Cl$;

or $3\,(KO, CrO_3) + 3\,NaCl + 6\,SO_3 = 3\,(KO, SO_3) + 3\,(NaO, SO_3) + CrCl_3 + 2\,CrO_3$. It distils over as a deep-red fuming liquid, which decomposes water, producing hydrochloric and chromic acids. It sets fire to phosphorus and many other combustible bodies. When its vapour is passed through a red-hot tube it is resolved into oxygen, chlorine, and sesquioxide of chromium, $2\,CrO_2Cl = Cr_2O_3 + O + Cl_2$; or $2\,(CrCl_3 + 2\,CrO_3) = 3\,Cr_2O_3 + O_3 + Cl_6$. Its constitution is uncertain, as, according to the two formulæ above given, it may be viewed either as chromic acid, in which 1 eq. of oxygen is replaced by chlorine, or as a compound of 1 eq. terchloride of chromium, and 2 eqs. chromic acid.

c. Perfluoride of Chromium.

When a mixture of chromate of lead, fluoride of calcium, and oil of vitriol, or, better, fuming sulphuric acid, is distilled in a silver retort, there is disengaged a red gas, which, in contact with the moisture of the air, produces hydrofluoric and chromic acids. Its precise composition is unknown. It was formerly considered a terfluoride; but it appears that this is not the case, and that it is more probably a quintofluoride, CrF_5. Possibly it may be, like the preceding compound, an oxyfluoride.

35. VANADIUM. $V = 68{\cdot}5$.

This very rare metal is found in small quantity in the slag of the iron furnaces where the iron ore of Taberg, in Sweden, is smelted, also in the lead mines of Scotland, as vanadiate of lead, a mineral which likewise occurs in Mexico. The metal is brittle, very infusible, and nearly silver white. In its chemical relations it is somewhat analogous to chromium; and, like it, forms coloured compounds. It is not oxidised either by air or water, and the only acid that dissolves it is aqua regia.

a. Protoxide of Vanadium. $VO = 76{\cdot}513$.

A black powder, which being heated burns into deutoxide.

b. Deutoxide of Vanadium. $VO_2 = 84{\cdot}526$.

This oxide, when anhydrous, is black, but forms blue salts; these are apt to become first green and then red, from the formation of vanadic acid.

c. Vanadic Acid. $VO_3 = 92{\cdot}539$.

Is obtained from vanadiate of lead by dissolving it in nitric acid, and precipitating lead and arsenic by sulphuretted hydrogen, which reduces the acid to deutoxide. The blue solution is evaporated, during which vanadic acid is reproduced, and the dry mass is digested in ammonia, which dissolves the acid. Into this solution a lump of sal-ammoniac is introduced, and, as this dissolves, the vanadiate of ammonia separates, being insoluble in a saturated solution of sal ammoniac. When this salt is heated to a point below red-heat in an open vessel, the ammonia is expelled, and vanadic acid left, which melts below a red-heat, and on cooling forms beautiful red crystals. With bases it forms salts which are either red or yellow, according as they are acid or neutral salts. It is singular that the neutral vanadiates of the alkalies may occur both yellow and colourless without any known difference in composition. Vanadic acid unites with deutoxide of vanadium, forming compounds which are purple, green, yellow, or orange, according as the acid or oxide predominates. Vanadic acid is distinguished from chromic acid by yielding a blue solution, when deoxidised, instead of a green one.

With chlorine, vanadium forms a bichloride, $V\,Cl_2$, and a terchloride, $V\,Cl_3$. The latter is formed by passing chlorine over a mixture of protoxide of vanadium and charcoal, heated to low redness, when the terchloride distils over as a yellow fuming liquid, which decomposes water, producing hydrochloric and vanadic acids. When this chloride is exposed to a current of ammonia, a white compound is formed, and if this be heated in a continued current of ammonia, metallic vanadium is formed, and adheres to the tube.

36. MOLYBDENUM. $Mo = 47{\cdot}7$.

This metal occurs in nature, combined with sulphur, forming a lead-coloured metallic mineral in broad plates or leaves, called molybdena, or sulphuret of molybdenum. It is found more sparingly as molybdic acid combined with lead. The metal may be obtained by passing hydrogen gas over molybdic acid, heated to whiteness in a porcelain tube. It is a brittle white metal, almost quite infusible. It forms three oxides.

MOLYBDENUM AND OXYGEN.

a. Protoxide of Molybdenum. $Mo\,O = 55{\cdot}713$.

A black powder, which, when heated in the air, takes fire and forms deutoxide. Its hydrate dissolves in acids.

b. Deutoxide of Molybdenum. $Mo\,O_2 = 63{\cdot}726$.

A dark-brown powder, forming a rust-coloured hydrate, which dissolves in acids, forming red salts. When exposed to air, it absorbs oxygen and becomes blue on the surface. The blue compound is a bimolybdate of the deutoxide, MoO_2, $2\,Mo\,O_3$.

c. Molybdic Acid. $Mo\,O_3 = 71{\cdot}739$.

Obtained by roasting the sulphuret at a low red-heat, as long as sulphurous acid escapes, and acting on the residue with ammonia, which dissolves molybdic acid. The molybdate of ammonia is then purified by crystallisation; and on heating it gently in an open platinum crucible, ammonia is expelled, and molybdic acid left. It is a white powder, fusible at a red-heat, which sublimes in a current of air. It is sparingly soluble in water. It forms salts with bases, which are colourless.

MOLYBDENUM AND CHLORINE.

The protochloride, $Mo\,Cl$, is a nearly black soluble compound. When chlorine gas is passed over metallic molybdenum gently heated, bichloride of molybdenum, $Mo\,Cl_2$, is formed as a deep red vapour, which condenses in black crystals, like iodine. When the deutoxide is heated in dry chlorine, there is formed a yellowish-white crystalline sublimate, which is an oxychloride, analogous to that of chromium, $Mo\left\{\begin{matrix}O_2\\Cl\end{matrix}\right.$ or $Mo\,Cl_3 + 2\,Mo\,O_3$.

MOLYBDENUM AND SULPHUR.

There are 3 sulphurets of this metal. 1. The bisulphuret, MoS_2, which is the usual ore of molybdenum already described; 2. The tersulphuret, a dark-brown or black powder, $Mo\,S_3$; 3. The persulphuret, also a dark powder, $Mo\,S_4$. Both the last are sulphur acids, combining with sulphur bases, such as sulphuret of potassium.

37. TUNGSTEN. $W = 99{\cdot}7$.

SYN. *Wolfram*—Occurs in nature, chiefly in the mineral wolfram, oxidised along with oxides of iron and manganese, and more sparingly in the mineral tungsten, a compound of tungstic acid with lime. The metal may be obtained as the preceding, but is little known. It is very infusible, and has the Sp. G. 17·4. When heated in air, it burns and forms tungstic acid.

TUNGSTEN AND OXYGEN.

a. Deutoxide of Tungsten. $WO_2 = 115{\cdot}726$.

To obtain it, 1 part of finely-powdered wolfram is fused in a platinum crucible with 2 parts of carbonate of potash. Tungstate of potash is formed, which is dissolved, filtered to separate the oxides of iron and manganese, and evaporated to dryness. The salt is mixed, in solution, with half its weight of sal-ammoniac, and the mixture dried up and ignited. The tungstic acid is reduced to the state of oxide by the ammonia, and chloride of potassium is formed; the latter is dissolved out by water, and the former, being first boiled with potash to remove any tungstic acid, and then washed and dried, is pure oxide of tungsten. It is a very heavy black powder, which, when heated in the air, burns like tinder, forming tungstic acid.

b. Tungstic Acid. $WO_3 = 123{\cdot}739$.

It is formed, as above, by heating the oxide in the air. It is a yellow powder, insoluble in water. With bases, it forms crystallisable salts. When heated to 500° or 600° in a current of hydrogen, it becomes of a fine deep blue, losing so much oxygen that it leaves an oxide, the blue oxide of tungsten, the formula of which is $W_2O_5 = WO_2 + WO_3$; so that it may be viewed as a tungstate of tungsten.

TUNGSTEN AND CHLORINE.

When heated in chlorine gas, tungsten forms two chlorides, a bichloride, WCl_2, and a terchloride, WCl_3. Both are red, volatile, and crystallisable compounds, subliming in beautiful crystals. The former, with water, produces hydrochloric acid and binoxide of tungsten; the latter yields hydrochloric acid and tungstic acid.

When the binoxide is heated in chlorine gas, there is formed an oxychloride in the shape of white volatile scales, like boracic acid. It is $WCl_3 + 2\,WO_3$; or $W\begin{cases}O_2\\Cl\end{cases}$.

The sulphurets of tungsten have no peculiar interest.

38. Columbium. $Ta = 185$.

Syn. *Tantalum.*—It occurs very sparingly, in the minerals tantalite and yttro-tantalite, as columbic acid. The metal is obtained by the action of potassium on the double fluoride of columbium and potassium, as a black powder, which, when compressed, exhibits metallic lustre; and when heated burns in air, yielding columbic acid.

With oxygen it appears to form two compounds; a binoxide, $Ta\,O_2$, and columbic acid, $Ta\,O_3$. The latter is a white insoluble powder, which forms salts with bases.

With chlorine it forms a volatile terchloride, $Ta\,Cl_3$; and with fluorine, a white soluble terfluoride, $Ta\,F_3$.

Rose is at present occupied with the study of two new metals found in the ores of Columbium or Tantalum, to which he has given the names of Pelopium and Niobium.

39. ANTIMONY. $Sb = 64{\cdot}6$.

This valuable metal is chiefly found in the mineral called antimony, which is a sesquisulphuret, $Sb_2\,S_3$, and which occurs both pure and combined with other sulphurets. From the sulphuret the metal is easily obtained by heating it with iron filings, when the sulphur combines with the iron, and the melted antimony collects at the bottom of the crucible.

It is a brittle metal, of Sp. G. 6·7, having a bluish or greyish-white colour when pure. It melts at 810°, and in a very intense heat it is volatilised. When heated strongly in open vessels, it takes fire, burning with a white light, and producing white vapours, which often condense in crystals, and are sesquioxide of antimony, $Sb_2\,O_3$. Antimony is the chief ingredient in type metal.

ANTIMONY AND OXYGEN.

a. Sesquioxide of Antimony. $Sb_2\,O_3 = 153{\cdot}239$.

To prepare it, sesquisulphuret of antimony is boiled with about 5 parts of strong hydrochloric acid, when sulphuretted hydrogen is given off, and sesquichloride of antimony is dissolved. $Sb_2\,S_3 + 3\,H\,Cl = Sb_2\,Cl_3 + 3\,HS$. The solution is now thrown into a large quantity of water, when a curdy precipitate separates, which is sesquioxide of antimony, combined with some undecomposed chloride, $9\,Sb_2\,O_3 + 2\,Sb_2\,Cl_3$, the oxide having been formed by the action of water on the chloride; $Sb_2\,Cl_3 + 3\,HO = Sb_2\,O_3 + 3\,H\,Cl$. The precipitate of oxychloride, which soon changes into crystals, if left in the liquid, is now to be washed and digested with an excess of carbonate of soda, by which the remaining chloride is converted into oxide. $Sb_2\,Cl_3 + 3\,Na\,O = Sb_2\,O_3 + 3\,Na\,Cl$. The sesquioxide is now pure, and is to be washed and dried.

It is a greyish-white heavy powder, fusible at a dull red-heat in close vessels, and volatile at a higher temperature. If heated in the open air it absorbs oxygen, forming antimonious acid. It is a base, and forms salts with acids, the most important of which is tartar emetic. Most of its soluble salts are decomposed by the contact of water.

Sesquioxide of antimony in solution is easily recognised by the peculiar brownish orange precipitate caused by sulphuretted hydrogen.

b. Antimonious Acid. $Sb_2 O_4 = 161{\cdot}252$.

When oxide of antimony is heated, it absorbs oxygen, and when antimonic acid is heated, it loses oxygen, the product in both cases being the permanent antimonious acid. It is a white insoluble powder, very infusible and fixed in the fire. It forms salts, called antimonites, with bases.

c. Antimonic Acid. $Sb_2 O_5 = 169{\cdot}265$.

Is formed by acting on the metal with strong nitric acid till it is converted into a white powder, which is hydrated antimonic acid. It is decomposed by a red-heat, yielding water, oxygen, and antimonious acid. It forms salts, called antimoniates, with bases.

All the oxides of antimony are used in medicine; but the sesquioxide is the most important, as the basis of tartar emetic, which is a double tartrate of potash and sesquioxide of antimony.

ANTIMONY AND CHLORINE.

a. Sesquichloride of Antimony. $Sb_2 Cl_3 = 235{\cdot}46$.

Is readily obtained by dissolving 1 part of sulphuret of antimony in 5 parts of hydrochloric acid (see above), and distilling the solution, until the volatile part becomes semisolid on cooling; the receiver is then changed, and what passes over afterwards is pure anhydrous chloride of antimony. It is a soft deliquescent solid, formerly called butter of antimony. When mixed with water, it is decomposed as mentioned above.

b. Perçhloride of Antimony. $Sb_2 Cl_5 = 306{\cdot}3$.

Obtained by acting on metallic antimony, or on the sesquichloride, with an excess of chlorine. It is also formed when powdered antimony is introduced into chlorine gas, when it burns with a vivid light. It is a colourless, volatile fuming liquid, which is decomposed by water, yielding hydrochloric and antimonic acids.

c. Oxychloride of Antimony. $9\,Sb_2O_3 + 2\,Sb_2Cl_3$.

This is the white powder formed when sesquichloride of antimony is thrown into water, as above described, under the head of sesquioxide. It soon changes into crystals, and is a definite compound of oxide and chloride. It is entirely converted into oxide by alkalies. It was formerly called powder of Algaroth.

Bromine and antimony combine readily, and form a volatile crystalline solid.

ANTIMONY AND SULPHUR.

a. Sesquisulphuret of Antimony. $Sb_2S_3 = 177{\cdot}5$.

This is the common ore of antimony, and is generally a dark-grey radiated fusible crystalline mass, Sp. G. 4·62. When formed by the action of sulphuretted hydrogen on salts of antimony, it is precipitated as a hydrate, of a brownish orange colour.

b. Persulphuret of Antimony. $Sb_2S_5 = 209{\cdot}7$.

When sesquisulphuret and sulphur are boiled in solution of potash, and an acid added to the filtered liquid, a golden-yellow precipitate is formed, often called the golden sulphuret of antimony, which is the persulphuret, Sb_2S_5.

c. Oxysulphuret of Antimony. $2\,Sb_2S_3 + Sb_2O_3 = 508{\cdot}2$.

This compound is found in nature as red antimony; and when sesquisulphuret of antimony is boiled with potash, and an acid added to the filtered liquid, a reddish orange precipitate is formed, which is often oxysulphuret; although it may be obtained nearly free from oxide, and is then hydrated sesquisulphuret. This is the substance so long known as mineral kermes; and it is the form in which sulphuret of antimony is chiefly used in medicine on the Continent. In this country we use the precipitated sesquisulphuret.

40. Uranium. $U = 217$.

This metal occurs in the form of protoxide, along with other oxides in the mineral pitchblende; and in that of peroxide in uranite and uran mica. When an excess of pitchblende is digested with diluted nitric acid, uranium dissolves, to the exclusion of iron, and after lead, copper, bismuth, or arsenic, have been removed by sulphuretted hydrogen, the solution may be considered pure. Carbonate of ammonia precipitates the peroxide of uranium, but an excess re-dissolves it; and this solution, if boiled, deposits pure peroxide of uranium, of a very fine yellow colour. The metal is little known; and from recent researches it would appear that what was supposed to be the metal is an oxidised body, acting, according to Péligot, the part of a metal; while, according to others, it is the protoxide of the true metal. In the present state of our knowledge, it is not easy to decide; and as the metal is not one of great importance, I shall not enter into details here; merely stating, that the oxide formerly called protoxide, is used for giving a fine black in painting on porcelain; and that the peroxide and all its compounds have rich and permanent yellow colours. Its solutions are yellow, and give with ferrocyanide of potassium, a rich chestnut-brown precipitate.

41. Cerium. 42. Lantanium.

These metals are in a state of still greater uncertainty. They occur invariably associated in some very rare minerals, and are not yet known in a state of purity. This applies to the oxides likewise. According to the most recent researches of Mosander, who discovered lantanium, these two metals appear to be always associated with a third, didymium, which is not yet fully described. It would be absurd at present to give a description which would infallibly have to be altered in a very short time. All these metals are too rare to become of any practical interest.

43. Bismuth. $Bi = 71 \cdot 07$.

Occurs sometimes as metal, more frequently as sulphuret. It is a highly crystalline metal, of a reddish-white colour, fusible at 476°, and even volatile in close vessels. When heated in the air it burns with a bluish flame, forming oxide of bismuth. Bismuth is an ingredient in Newton's fusible metal, and in various fusible alloys.

BISMUTH AND OXYGEN.

a. Protoxide of Bismuth. $Bi\,O = 79.083$.

To obtain it, bismuth is dissolved in nitric acid, and the solution thrown into water, when a copious white precipitate of subnitrate of bismuth is formed. This is washed, dried, and ignited, and protoxide of bismuth is left. It is a yellow powder, fusible at a red heat. With acids it forms colourless salts. Most of these salts are decomposed when thrown into water; and this character, coupled with the black caused by sulphuretted hydrogen, enables us easily to recognise the presence of bismuth, and to separate it from other metals.

b. Peroxide of Bismuth. $Bi_2 O_3 = 166·179$.

Formed when protoxide of bismuth is fused with hydrate of potash, or when it is digested in a solution of chloride (hypochlorite) of soda. It is a heavy brown powder, of a neutral character.

Chloride of Bismuth. $Bi Cl = 106·42$.

Powdered bismuth takes fire in chlorine gas, and forms a grey semisolid chloride, not volatile, the old butter of bismuth.

Bromide of bismuth resembles iodine in appearance; it is fusible and volatile.

The sulphuret of bismuth found in nature is of a lead-grey colour; that formed by the action of sulphuretted hydrogen on the salts of bismuth is black. It is a protosulphuret, $Bi S$.

44. TITANIUM. $Ti = 24·3$.

This metal is found oxidised in several minerals; and occurs occasionally in the metallic form, in the slag of iron works, as small cubical crystals, exactly similar to copper in appearance, of Sp. G. 5·3, and very infusible. When heated with nitre, they are oxidised, producing titanic acid.

TITANIUM AND OXYGEN.

a. Protoxide of Titanium. $Ti O$?

When a solution of titanic acid in hydrochloric acid is acted on by zinc, a purple powder is thrown down, which is supposed to be a hydrate of the protoxide. It rapidly absorbs oxygen from the air, and is reconverted into titanic acid.

b. Titanic Acid. $Ti O_2 = 40·326$.

To obtain this acid, rutile, which is a native titanate of iron and manganese, is heated to strong redness in a porcelain tube, and sulphuretted hydrogen gas passed over it, which acts on the oxides of iron and manganese, converting them into sulphurets; the operation is continued as long as water is formed, and the residue is digested in hydrochloric acid, which dissolves the sulphurets, leaving the titanic acid, mixed with a little sulphur. Should it not appear quite white, the process is repeated.

Titanic acid is a snow-white infusible solid, in its relations somewhat analogous to silicic acid. When it has been fused with alkali, it becomes soluble in strong hydrochloric acid, but it is precipitated by boiling. A solution of galls causes an orange-red colour in its solution, and a rod of zinc causes a purple deposit. Titanic acid is used in making the finer kinds of enamel for artificial teeth, from its whiteness and hardness.

BICHLORIDE OF TITANIUM.

Formed by passing chlorine gas over metallic titanium, or a mixture of titanic acid and charcoal, at a red-heat. It is a transparent colourless liquid, boiling at a little above 212°, and fuming strongly in the air. When a few drops of water are added to a portion of it, a very violent action takes place, and a solid hydrate of titanic acid is left, hydrochloric acid being given off. $Ti\,Cl_2 + 2\,HO = Ti\,O_2 + 2\,H\,Cl$. It absorbs a large quantity of ammonia, and yields a solid compound.

Bisulphuret of titanium is formed by passing the vapour of bisulphuret of carbon over titanic acid, at a white-heat. $C\,S_2 + Ti\,O_2 = C\,O_2 + Ti\,S_2$. It forms thick, green masses, which become yellow and metallic-looking by friction.

45. Tellurium. $Te = 64{\cdot}2$.

This very rare metal occurs alloyed with gold and silver. It has a colour between that of tin and lead, is very brittle, and has the Sp. G. 6·2578. It is very fusible, and volatile at a red-heat. It forms two oxides. The first, oxide of tellurium, or tellurous acid, $Te\,O_2$, is analogous to selenious acid, and like it formed by the action of nitric acid on the metal. It is a white insoluble powder, which forms with the alkalies crystallisable salts, from which it is separated by acids as a flaky hydrate, which dissolves in acids, and even in water. It is blackened by sulphuretted hydrogen, and reduced to the metallic state by zinc and other metals. The other oxide is telluric acid, $Te\,O_3$, which is formed when tellurium is deflagrated with nitre. It is a soluble and crystallisable acid; the crystals are $Te\,O_3, 3\,H\,O$. Its salts are not much known.

There are two chlorides: the protochloride, $Te\,Cl$, a black solid, yielding a violet vapour; and the bichloride, a white, volatile, crystallisable solid.

With sulphur, tellurium forms two compounds, one of which, the bisulphuret, $Te\,S_2$, is a dark-brown powder; the other is yellow, but not permanent.

With hydrogen, tellurium forms a gaseous compound, obtained by the action of hydrochloric acid on an alloy of tellurium with zinc. It is a feeble acid, analogous in composition, smell, and other characters, to sulphuretted hydrogen. With water it forms a claret-coloured solution, which precipitates many metallic salts, yielding precipitates which are tellurets of the metals, analogous to the sulphurets and seleniurets. Its formula is $H\ Te$, and its action on metallic oxides is $H\ Te + M\ O = M\ Te + H\ O$.

46. Copper. $Cu = 31{\cdot}6$.

This important metal is sometimes found as metal, but it chiefly occurs in copper pyrites, the sulphuret, and in blue copper ore, or malachite, which is carbonate of copper. The latter ore, heated with charcoal, yields the metal most easily. It is distinguished from all other metals, except titanium, by its red colour. It melts in a strong red-heat, and has the Sp. G. 8·667. It is both ductile and malleable, and has a high degree of tenacity. It is hard, elastic, and sonorous. Heated in the open fire it absorbs oxygen, and produces a black crust of oxide of copper, $Cu\ O$. Its proper solvent is nitric acid, but it dissolves in all acids if air be admitted, even in the cold. This renders its use for culinary purposes dangerous, as copper vessels left with vinegar, or any vegetable acid in them, are sure to be corroded, and the solutions are very poisonous. Copper is an ingredient of brass, in which it is combined with zinc; and of bronze and bell-metal, in which it is alloyed with different proportions of tin.

COPPER AND OXYGEN.

a. Protoxide of Copper. $Cu\ O = 39{\cdot}613$.

Syn. *Black Oxide of Copper*—Is obtained, as above, by heating copper in air, or by calcining nitrate of copper, when the oxide is left. It is a heavy black powder, which is a strong base, and forms with acids, salts, all of which are blue or green. The solutions of this oxide have generally a blue colour; they give with potash a pale-blue hydrate, becoming black when boiled in the liquid in which it was formed; with ammonia in excess a deep violet-blue solution; with sulphuretted hydrogen, a black; and with ferrocyanide of potassium, a chestnut-brown precipitate. The last test is highly delicate. Iron throws down metallic copper from these solutions. Black oxide of copper is not decomposed by heat, but has the valuable property of yielding all its oxygen at a red-heat to organic matter; hence its importance in organic analysis.

b. Suboxide of Copper. $Cu_2\ O = 71{\cdot}213$.

Syn. *Red Oxide of Copper*—Occurs native, and is formed when a mixture of dried sulphate of copper, dried carbonate of soda, and copper filings, is ignited strongly for 20 minutes. It is a red powder. It dissolves in hydrochloric acid, forming a colourless solution, from which alkalies precipitate an orange hydrate, but most acids resolve it into black oxide and copper. $Cu_2O = CuO + Cu$. It is a feeble base.

COPPER AND CHLORINE.

Chloride of Copper. $CuCl = 66{\cdot}02$.

Forms green deliquescent needles, which are a hydrate. The anhydrous chloride is yellow.

Dichloride of Copper. $Cu_2Cl = 98{\cdot}62$.

Is found when copper-filings are heated with 2 parts of corrosive sublimate. A resinous-like, fusible mass, of a yellow or brown colour.

Diniodide of Copper. $Cu_2I = 189{\cdot}7$.

Formed when iodide of potassium is added to a solution of 1 part of sulphate of copper, and 3 parts of sulphate of iron. It falls as a dirty white precipitate. We are thus enabled to precipitate the whole of the iodine from any iodide; for if we add only sulphate of copper, not more than one-half of the iodine is got, the other half being set free, because no protoiodide of copper exists.

Disulphuret of Copper. $Cu_2S = 79{\cdot}32$.

This is the native ore, copper pyrites, and is formed when sulphuretted hydrogen acts on solutions of copper.

The best antidote to the preparations of copper is white of egg, which forms with oxide of copper an inert compound.

47. LEAD. $Pb = 103{\cdot}6$.

This valuable metal chiefly occurs combined with sulphur, forming the mineral galena, or lead-glance, from which all the lead of commerce is obtained. It is also met with as carbonate, sulphate, phosphate, and arseniate of oxide of lead. The galena is roasted, to expel the sulphur and oxidise the lead, and the oxide is heated with charcoal to reduce the metal; indeed, a good deal of lead is obtained by heating the ore alone in a reverberatory furnace, where it is partly converted into sulphate of lead, and partly into oxide. Both of these act on undecomposed sulphuret, yielding sulphurous acid and metallic lead: thus $2PbO + PbS = SO_2 + Pb_3$: and, $PbO, SO_3 + PbS = 2SO_2 + Pb_2$.

Lead has a blueish-grey colour, and high lustre, but soon tarnishes. Its Sp. G. is 11·381. It is malleable, ductile, soft, and flexible, but of inferior tenacity. It melts about 612°. When heated in air it is rapidly oxidised, and, according to the heat, yields protoxide, or red oxide. The grey matter that forms on the surface of melted lead is a mixture of metal and protoxide.

Lead, when exposed to the action of air and moisture, is rapidly corroded, and particularly in contact with pure or rain-water, forming a white crust of carbonate, which is highly poisonous. The oxygen and carbonic acid are absorbed from the air. This renders lead quite improper for pipes or cisterns, where rain-water, or very soft water, is to be kept in them; but Dr. Christison has shown that lead is protected by the presence of a minute quantity of saline matter, particularly sulphates, and as these exist in hard-water, or even in such water as that of Edinburgh, in sufficient quantity, lead may be safely used in such cases, as it is not corroded, the surface becoming covered with an insoluble film, which protects the mass of the metal.

Lead is a most useful metal, not only in itself, but as an ingredient in pewter, solder, and other important alloys.

LEAD AND OXYGEN.

a. Protoxide of Lead. $PbO = 111{\cdot}613$.

Prepared by heating lead in air till it is entirely converted into a yellow powder, which is the protoxide, often called massicot. When partially fused, as in the process of cupellation, it is called litharge. It is a heavy, insoluble, yellow or reddish powder, which is a base, and forms with acids the salts of lead, which are generally colourless, and have a sweet taste. Their solutions give with potash a white hydrate, soluble in excess; with carbonates, a white carbonate, which is the paint, white lead; with sulphates, or sulphuric acid, a white insoluble sulphate; with iodide of potassium, a bright-yellow iodide of lead; with sulphuretted hydrogen, a dark-brown, nearly black sulphuret. Lead is very easily recognised in solution by the combination of the two tests of sulphuric acid, and sulphuretted hydrogen, or iodide of potassium and sulphuretted hydrogen.

b. Sesquioxide of Lead. $Pb_2O_3 = 231{\cdot}239$.

Is formed when solution of hypochlorite of soda is added to protoxide of lead dissolved in caustic soda. It is a reddish-yellow insoluble powder, resolved by acids into protoxide and oxygen.

c. Peroxide of Lead. $Pb\,O_2 = 119{\cdot}626$.

Prepared by acting on red oxide of lead (see below) with dilute nitric acid, which dissolves protoxide, and leaves peroxide of lead as a puce-coloured insoluble powder. It is also formed when litharge is fused with chlorate of potash at as low a heat as possible; and when chlorine is passed through a solution of acetate of protoxide (sugar of lead). Here, $2\,Pb\,O + Cl = Pb\,Cl + Pb\,O_2$. The peroxide yields oxygen when heated, or when acted on by acids, which combine with protoxide, liberating oxygen.

d. Red Oxide of Lead. $Pb_3\,O_4 = 342{\cdot}852$.

This well-known pigment is formed when lead is exposed to a current of air at 600° or 700°. It is formed either of protoxide and peroxide, $2\,Pb\,O + Pb\,O_2$; or of sesquioxide and protoxide, $Pb_2\,O_3 + Pb\,O$. Acids resolve it into peroxide and protoxide. It is much used in the manufacture of flint glass, to give brilliancy and fusibility to the glass.

Chloride of Lead. $Pb\,Cl = 39{\cdot}02$.

Is formed when hydrochloric acid or a soluble chloride is added to any solution of a salt of protoxide of lead. $H\,Cl + Pb\,O = Pb\,Cl + H\,O$. It is deposited in strong solutions as a white precipitate, sparingly soluble in cold water. It dissolves in hot water, and forms white needles on cooling. It is fusible below a red-heat, and forms on cooling a horny mass.

Iodide of Lead. $Pb\,I = 229{\cdot}9$.

Formed when hydriodic acid or a soluble iodide is added to a salt of protoxide of lead, $K\,I + Pb\,O, N\,O_5 = Pb\,I + K\,O, N\,O_5$. It forms a bright-yellow very sparingly soluble precipitate, which dissolves in hot water, forming a colourless solution; and, on cooling, deposits beautiful yellow six-sided tables with the lustre of gold.

Bromide of lead, $Pb\,Br$, resembles the chloride.

Sulphuret of Lead. $Pb\,S = 119{\cdot}7$.

This is the native compound from which the lead of commerce is obtained. It is grey, and has a high metallic lustre, and is often found beautifully crystallised in cubes. By the action of fuming nitric acid, it is entirely converted into sulphate of lead. $Pb\,S + 4\,N\,O_5 = Pb\,O, S\,O_3 + 4\,N\,O_4$. It is formed by the action of sulphuretted hydrogen on the salts of lead, as a black powder.

ORDER 3.—METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY A RED-HEAT.

48. MERCURY. $Hg = 202$.

This metal is distinguished from all others by its being liquid at ordinary temperatures. It is occasionally found in the metallic state; but its usual ore is the bisulphuret, known as cinnabar. From this it is obtained by distilling it in iron vessels with iron filings.

The appearance of mercury or quicksilver is well known. Its Sp. G. is 13·545 at 47°: but it contracts in freezing; and as a solid, its Sp. G. is 15·612. It freezes at —39°, and boils about 620°. When heated to its boiling point along with air, it slowly combines with oxygen, forming a red powder, which is peroxide of mercury, the *oxydum hydrargyri rubrum per se* of the older chemists. At a somewhat higher temperature the oxygen again separates from the metal. The uses of mercury for barometers, thermometers, mirrors, &c., are universally known.

MERCURY AND OXYGEN.

a. Protoxide of Mercury. $Hg\,O = 210{\cdot}013$.

To prepare it, protochloride of mercury (calomel) is rapidly mixed with aqua potassæ in excess, by rubbing in a mortar; and the black powder formed is washed with cold water and dried in the dark. $Hg\,Cl + K\,O = K\,Cl + Hg\,O$. It is a black or dark olive powder, which is easily resolved into peroxide and metal O $2\,Hg\,O = Hg\,O_2 + Hg$; and hence is difficult to keep. It is a feeble base, and forms with acids crystallisable salts, such as the acetate and nitrate. Its solutions are precipitated black by caustic alkalies; white (calomel) by hydrochloric acid, or a soluble chloride; and the metal is reduced by copper, phosphorous acid, or protochloride of tin.

b. Peroxide of Mercury. $Hg\,O_2 = 218{\cdot}026$.

Is formed, as above mentioned, by the combined action of heat and air; but much more readily by dissolving mercury in nitric acid, evaporating to dryness, and heating the dry residue as long as any nitrous acid is given off. The peroxide is left in the form of a crystalline scaly powder, nearly black while hot, but of a light-red when cold. In this form it is often called red precipitate, a most absurd name, as it has not been prepared by precipitation, and when precipitated it appears as a yellow hydrate. It is a base, and forms salts with acids, which are apt to be decomposed by hot water, yielding insoluble yellow sub-salts and soluble super-salts. These salts give a yellow precipitate with caustic potash, a white with ammonia, and a fine scarlet with iodide of potassium; phosphorous acid, protochloride of tin, and copper, reduce the mercury to the metallic state.

Both the oxides of mercury, in their solutions, are precipitated black by sulphuretted hydrogen.

MERCURY AND CHLORINE.

a. Protochloride of Mercury. $Hg\,Cl = 237{\cdot}42$.

SYN. *Calomel*—Occurs sparingly as horn quicksilver in the mineral kingdom. May be prepared either by subliming a mixture of bichloride of mercury and mercury, $Hg\,Cl_2 + Hg$, which yields $2\,Hg\,Cl$; or by adding hydrochloric acid or solution of common salt to a solution of protonitrate of mercury, when the protochloride is precipitated. $Hg\,O, NO_5 + Na\,Cl = Na\,O, NO_5 + Hg\,Cl$. It is a heavy white volatile powder, insoluble in water. It is blackened by alkalies. When first prepared, it is always contaminated with corrosive sublimate, and must be well washed with hot water before it is used as a medicine.

b. Bichloride of Mercury. $Hg\,Cl_2 = 272{\cdot}84$.

SYN. *Corrosive Sublimate.*—This compound is formed when mercury is heated so as to burn in chlorine gas. It is prepared by subliming a mixture of bisulphate of peroxide of mercury with common salt. $Hg\,O_2, 2\,S\,O_3 + 2\,Na\,Cl = 2\,(Na\,O, S\,O_3) + Hg\,Cl_2$. Or it may be formed by dissolving peroxide of mercury in hydrochloric acid, when it is deposited in crystals. It is a heavy, translucent, crystalline, volatile solid, soluble in 20 parts of cold water, and in two parts of hot water. It has a very disagreeable acrid, metallic taste, and is very poisonous. Its solution gives, with fixed alkalies, a yellow precipitate of hydrated peroxide; with ammonia, a white insoluble powder, called white precipitate; with sulphuretted hydrogen, first a white, and when the test is added in excess, a black precipitate of sulphuret; with iodide of potassium, a scarlet precipitate of periodide; and with protochloride of tin, a grey powder of running mercury.

The proper antidote to corrosive sublimate, as a poison, is albumen or white of egg, which forms with it an insoluble and inert compound.

MERCURY AND IODINE.

a. Protoiodide of Mercury. $Hg I = 328{\cdot}3$.

This compound is formed when iodine and mercury are rubbed together in the proper proportions, with a little alcohol, which facilitates the combination; or when iodide of potassium is added to solutions of protoxide of mercury; $Hg O + K I = K O + Hg I$. It is a greenish-yellow, heavy insoluble powder, which may be sublimed; but is apt to be decomposed by heat, and especially by light, into metallic mercury and periodide, $2 Hg I = Hg I_2 + Hg$.

b. Biniodide of Mercury. $Hg I_2 = 454{\cdot}6$.

Syn. *Periodide of Mercury*—Is obtained by rubbing together iodine and mercury in the proper proportions, with a little alcohol, and subliming; or by adding iodide of potassium to a solution of corrosive sublimate. $Hg Cl_2 + 2 K I = 2 K Cl + Hg I_2$. It is an insoluble powder, of the most brilliant scarlet colour, superior to that of vermilion, and equal to that of certain flowers, such as *lobelia cardinalis*, *salvia splendens*, and certain varieties of *pelargonium*: but unfortunately it loses part of its brilliancy when exposed to light under certain circumstances. Although insoluble in water, it dissolves easily in an excess of either of its precipitants; a hot solution of nitrate of peroxide of mercury dissolves it, and on cooling, deposits it in beautiful red crystals.

The biniodide, when heated, undergoes a remarkable change: the red powder, which has an earthy aspect, passing into yellow crystals; and when further heated, melting and subliming in large yellow rhombic tables. Either these, or the yellow crystalline powder first mentioned, sometimes retain their yellow colour pretty long; but agitation, or friction, or the mere touch of a sharp point, at once causes them to become red, beginning at a point or points, and gradually changing throughout the mass. This is the result entirely of a new molecular arrangement; for the composition of the red and yellow iodide is precisely the same.

The bromides of mercury are very similar to the chlorides.

MERCURY AND SULPHUR.

a. Protosulphuret of Mercury. $Hg S = 218{\cdot}1$.

Formed by the action of sulphuretted hydrogen on diluted protonitrate of mercury. It is a black powder which, by heat, is resolved into metallic mercury and bisulphuret.

b. Bisulphuret of Mercury. $Hg\ S_2 = 234{\cdot}2$.

Occurs naturally, as cinnabar, and is the chief ore of mercury. Is formed by fusing sulphur with 6 parts of mercury, and subliming; or by pouring a solution of corrosive sublimate into an excess of hydrosulphuret of ammonia, when a black powder falls, which is to be dried and sublimed. When sublimed, the bisulphuret forms a dark-red crystalline mass, called cinnabar, which, when finely powdered, acquires a very fine red colour, and becomes vermilion.

The black powder obtained by triturating together equal parts of mercury and sulphur, and long known as Ethiops mineral, is a mixture of sulphur with bisulphuret. It is to be observed, that the bisulphuret, like the biniodide, exists in two states, being sometimes black, and sometimes red.

49. SILVER. $Ag = 108{\cdot}31$.

This beautiful and useful metal is found in the metallic state; also, as chloride and as sulphuret. It occurs also alloyed with gold, tellurium, antimony, copper, and arsenic. Almost all varieties of galena (the ore of lead) contain a small proportion of sulphuret of silver; and in many places, it is found worth while to extract this silver from the lead smelted from the ore. The separation of lead from silver is effected by cupellation; that is, by heating the alloy in a current of air, when the lead is oxidised, and the oxide is either absorbed by the cupel or porous cup; or, on the large scale, is raked away to the side, while the silver remains as a bright metallic globule, or button. From the ore in which silver occurs as metal, it is extracted by amalgamation with mercury; and the amalgam being distilled, leaves pure silver.

When the proportion of silver in lead is very small, it may be still rendered available by melting the lead, and allowing it to crystallise; the crystals which form are pure lead, and as these are separated, the silver gradually accumulates in the fluid portion. This at last comes to be very rich in silver, and is cupelled apart to obtain the latter metal.

Silver has a fine white colour and high lustre. It is highly malleable and ductile, and, when pure, is a soft metal. Its Sp. G. is 10·5; it melts at a full red-heat, and when melted in open vessels, it absorbs a considerable quantity of oxygen, without apparently combining with it; and on consolidating, gives out the whole, causing the metal to assume a beautiful frosted aspect. The uses of silver are quite familiar. For the purpose of making coinage, or silver plate, it is alloyed in this country with rather less than $\frac{1}{12}$ of copper, which renders it much harder and fitter for wear.

When silver, as commonly happens, has been alloyed with copper, it is purified in several ways. 1. By dissolving the alloy in nitric acid, and adding common salt, which throws down the silver as chloride; and from this the metal is separated (see below). 2. By dissolving the alloy in oil of vitriol, with the aid of heat, and acting on the hot solution with metallic copper, which precipitates the silver as metal, the copper taking its place in the solution. In both processes, the small quantity of gold usually present in commercial silver, is left by the acid as a black powder, when the silver and copper are dissolved; and its extraction generally covers the whole expense of the purification of the silver, leaving, besides, a profit to the purifier.

Oxide of Silver. $AgO = 116{\cdot}323$.

This, the only oxide of silver, is obtained by dissolving silver in nitric acid, and adding caustic potash, when the oxide is precipitated as a brown powder. It may also be formed by boiling the moist, recently-prepared chloride with very strong potash, when it appears as a very dense pure black powder. It is a base, and neutralises all acids, forming salts, most of which are insoluble, or sparingly soluble. The oxide is reduced to the metallic state by a red-heat. Its solutions are easily recognised. They give, with caustic fixed alkalies, a brown precipitate; with ammonia, a similar one, soluble in the slightest excess; with hydrochloric acid, or any soluble chloride, the white curdy precipitate of chloride of silver, insoluble in water and acids, but soluble in ammonia; and with sulphuretted hydrogen, a dark-brown, nearly black precipitate of sulphuret. Silver and all its compounds are very sensitive to sulphuretted hydrogen, which blackens them. Most of the compounds of oxide of silver are very soluble in ammonia; and all the compounds of silver are darkened by the action of light, a property which has lately been applied to useful purposes in the Daguerréotype, Calotype, and other photographic methods. Oxide of silver is reduced to the metallic state from its solutions by copper, zinc, and several other metals. When mercury is used, there is formed a beautiful arborescent crystallisation of an alloy of silver and mercury, called Arbor Dianæ.

When precipitated oxide of silver is acted on by ammonia, a dark powder is formed, which fulminates violently when heated, or by friction. Its composition is not exactly known; but it probably contains a compound of silver with nitrogen.

Chloride of Silver. $Ag\,Cl = 143 \cdot 78$.

Is found in the mineral kingdom as horn silver; and is formed whenever oxide of silver comes in contact with chlorine, hydrochloric acid, or a soluble chloride. $Ag + OH$ Cl (or $M\,Cl$)$=Ag\,Cl + HO$ (or MO). It then forms a heavy white curdy precipitate, quite insoluble in water and acids, but soluble in ammonia. Hence, a solution of silver is a most delicate test for hydrochloric acid, or chlorides. The chloride melts at a heat below 600°, and, on cooling, forms a translucent horny mass. The freshly precipitated chloride is very sensitive to light, and this is the foundation of Talbot's Calotype.

To reduce the chloride to the metallic state, several methods are followed. 1. It is covered with water acidulated with hydrochloric acid, and a rod of zinc is introduced, which gradually reduces the whole mass of chloride. $Ag\,Cl + Zn = Ag + Zn\,Cl$. The silver is digested in dilute hydrochloric acid, washed, dried, and fused. 2. The dried chloride is fused with carbonate of potash; when carbonic acid and oxygen are given off, chloride of potassium is formed, and metallic silver collects as a button in the bottom of the crucible. In this process, the effervescence is troublesome: and if the heat be not high enough, the silver remains disseminated in the mass; while, if the heat be too high, the crucible is corroded, and the silver flows into the fire. Hence this process, although it succeeds in experienced hands, is very apt to fail in those of beginners, for which reason I have proposed the following. 3. The freshly precipitated chloride, while still moist, is boiled with very strong caustic potash, till it is converted into black oxide of silver entirely, or in great part. The oxide is then heated with a little pearlash and borax, and yields a button without any risk of failure. The oxide thus prepared, answers admirably for making pure nitrate of silver, as diluted nitric acid dissolves it instantly, leaving undissolved any undecomposed chloride. The action of the potash in the two last processes is very simple: $Ag\,Cl + KO = K\,Cl + Ag\,O$.

Iodide of Silver. $Ag\,I = 234 \cdot 88$.

Formed under the same circumstances as chloride of silver, which it resembles. It is a yellowish-white insoluble powder, insoluble in water, and nearly so in ammonia. It is very sensitive to light, and a film of iodide of silver is the substance which receives the impressions in the silver plates of the Daguerréotype.

The bromide of silver is very similar to the chloride.

Sulphuret of Silver. $Ag\,S = 124{\cdot}43$.

Occurs as a mineral, silver glance, and is formed by the action of sulphuretted hydrogen on oxide of silver, or indeed on silver itself, or any compound of it whatever. Polished silver is instantly tarnished by the minutest trace of sulphuretted hydrogen, so that coal-gas, which contains a mere trace of that gas, cannot be used in silversmiths' shops. It would appear that the affinity of silver for sulphur is very powerful.

50. GOLD. $Au = 199{\cdot}2$.

This metal is found native, either pure, or alloyed with silver and tellurium. When combined with silver, it is purified by quartation; that is, by fusing it with so much silver, that the gold does not exceed one-fourth of the mass, and then acting on the alloy by nitric acid, which dissolves the silver, and leaves the gold as a black or brown powder, which, when fused, assumes the peculiar yellow colour of gold.

Gold is distinguished by its pure yellow colour, high metallic lustre, and great density. Its Sp. G. is 19·3. It is the most ductile and malleable of all metals; and it melts in a strong red or white heat. From its feeble affinities, gold does not readily tarnish, and may be heated for any time without change, except when it is exposed to a strong electric spark, when it burns with a green light. No single acid dissolves it; but it is easily dissolved by chlorine and by nitro-hydrochloric acid, or aqua regia, chlorine being apparently the solvent in both cases.

GOLD AND OXYGEN.

The oxides of gold can only be obtained by indirect means.

a. Protoxide of Gold. $Au\,O = 207{\cdot}213$.

Formed by the action of cold potash on protochloride of gold. It forms a green precipitate, which is soon resolved into peroxide and metallic gold.

b. Peroxide of Gold. $Au\,O_3 = 223{\cdot}239$.

Obtained by adding carbonate of potash to a neutral solution of perchloride of gold, as a brownish-yellow hydrate, which at 212° loses its water and becomes black. It is a very feeble base, having apparently a tendency to combine with bases rather than with acids. When acted on by ammonia it yields fulminating gold, a very dangerous compound, which probably, like fulminating silver, contains a compound of gold with nitrogen. A binoxide of gold, $Au\,O_2$, is supposed to exist, and to be formed as a purple powder when gold is burned by the electric spark.

GOLD AND CHLORINE.

a. Protochloride of Gold. $Au\,Cl = 234{\cdot}67$.

Formed by exposing the perchloride to a heat of 600°. It is a yellow insoluble powder, which by boiling in water is changed into metallic gold and perchloride. $3\,Au\,Cl = Au_2 + Au\,Cl_3$.

b. Perchloride of Gold. $Au\,Cl_3 = 305{\cdot}61$.

This, the usual form in which gold is dissolved, is formed when gold is acted upon by aqua regia or by chlorine. It forms, when evaporated sufficiently, ruby-red crystals, which are deliquescent. The solution is yellow. It is reduced to the metallic state by many deoxidising agents, such as protosulphate of iron, formic acid and formiates, &c. &c.; and when the reduction takes place in a diluted solution, the metallic gold appears as a blue powder as long as it is suspended in the liquid. Deoxidising agents probably act by decomposing water, the hydrogen of which deprives the gold of chlorine. Chloride of gold is also reduced directly by the action of hydrogen, phosphuretted hydrogen, and metals. When heated it is first reduced to protochloride and afterwards to metallic gold.

When solution of protochloride or sesquichloride of tin is added to solution of gold, a purple precipitate is formed, long known as the purple of Cassius, and used for staining glass. Its composition is not known with certainty, but it contains gold, tin, and oxygen.

The iodides of gold are in composition analogous to the chlorides. The sulphuret, formed by the action of sulphuretted hydrogen on the perchloride, is a black powder, supposed to be a tersulphuret, $Au\,S_3$.

51. PLATINUM. $Pt = 98{\cdot}84$.

This metal, like gold, is found in the metallic state, but always alloyed with other metals, and generally mixed, as the ore of platinum, in the form of sand, with gold, silver, and other minerals in small proportion. The purification of platinum is a tedious operation, too difficult to be described here in a few words. But the essential parts of the process are the dissolving the platinum ore in aqua regia; the precipitating the platinum as a double chloride of ammonium and platinum; and the igniting of this salt, which leaves pure platinum in a spongy state, containing, perhaps, a trace of iridium. The double chloride may also be reduced by the action of zinc and diluted sulphuric acid, when the platinum is obtained as a dense black powder. Spongy platinum is rendered malleable by being first exposed to powerful pressure, and then heated and hammered till it is rendered dense and workable. Or it may be fused before the oxyhydrogen blowpipe, being quite infusible in the furnace.

Pure platinum resembles silver, but is not so white. Its density is about 21·5, and it is both malleable and ductile, particularly the latter. It is not melted by any furnace-heat, nor acted on by air and heat together; hence its extreme utility to the chemist. When ignited with caustic alkalies, however, it is oxidised and corroded; and care should be taken never to heat any metal in vessels of platinum, as it readily forms alloys, and is much injured in consequence. The proper solvent of platinum is chlorine or aqua regia, but it dissolves less easily than gold.

One of the most important properties of platinum is its power of causing gases to enter into combination. When a current of hydrogen gas falls on spongy platinum or platinum powder in the air, combination between hydrogen and oxygen takes place at the surface of the platinum, and the heat developed is sufficient to make the metal red-hot. The red-hot metal, then acting like any other red-hot body, sets fire to the hydrogen. This power is present even in solid polished platinum; for if a perfectly clean plate of platinum be introduced into a mixture of oxygen and hydrogen, it will cause them to combine, and may, by becoming red-hot, even produce explosion. But the power is seen in greatest perfection in the black powder of platinum; and Döbereiner has shown that this powder contains within its pores about 250 times its volume of oxygen, which, as the pores do not exceed $\frac{1}{4}$ of the powder, must occupy no more than $\frac{1}{1000}$ of its bulk as gas, and must be denser than water. This explains the action on hydrogen. In the case of the polished metal it is supposed that the particles of the gases, which repel each other, are attracted by the metal, and consequently, on its surface, come within the sphere of affinity. The powder of platinum, by virtue of the oxygen in its pores, rapidly oxidises the vapour of alcohol into acetic acid, &c.; and the smallest portion of this powder introduced into a mixture of oxygen and hydrogen causes instantaneous explosion.

OXIDES OF PLATINUM.

Platinum appears to form a green protoxide, $Pt\,O$, and a rust-coloured binoxide, $Pt\,O_2$, which, when anhydrous, is nearly black; but these compounds are even more prone to change than the oxides of gold, and the binoxide is hardly to be obtained pure, owing to its tendency to combine with the alkalies used to precipitate it. Both oxides are prepared from the chlorides.

PLATINUM AND CHLORINE.

a. Protochloride of Platinum. $Pt\,Cl = 134{\cdot}31$.

Prepared by heating the bichloride to 450°, when the protochloride is left as a greenish-grey insoluble powder. This chloride enters into combination with ammonia, and the compound, under certain circumstances, gives rise to several very remarkable organic or quasi-organic bases, of which platinum is an element.

b. Bichloride of Platinum.

This, the usual soluble salt of platinum, is best made by dissolving spongy platinum in aqua regia, and gently evaporating to the consistence of syrup, when, on cooling, the whole forms a crystalline brownish-yellow mass, very soluble in water. The solution of platinum is characterised by yielding metallic platinum as a black powder when acted on by zinc and diluted sulphuric acid; and by giving with salts of potash and of ammonia a sparingly soluble yellow double chloride, which is also reduced by zinc and sulphuric acid.

The iodides and sulphurets of platinum correspond in composition to the chlorides, but are of no practical interest. The iodides are very dark-coloured, so that the addition of iodide of potassium to a solution of platinum produces a very intense reddish-brown colour, gradually becoming nearly black.

52. Iridium. $Ir = 98{\cdot}84$.

This is one of the metals which accompanies platinum. It occurs combined with osmium, alloyed with a large proportion of platinum, and occasionally nearly pure, but still containing platinum. Specimens have been found of Sp. G. 23 to 26, indicating that iridium is the heaviest of all metals. It is also the most infusible, the hardest, and that which resists best the action of acids. These latter properties would render it most valuable if it could be wrought, but as yet it has proved refractory. It is remarkably analogous to platinum, from which it chiefly differs in the darker colour of its choride, and of the double chlorides which it forms with potassium and ammonium. The latter occurs in very dark-red octohedral crystals, nearly black, which, when heated, leave metallic iridium, very similar to spongy platinum, and acting in the same way on hydrogen.

Iridium forms 4 oxides and 4 chlorides, which are little known. They have different colours; hence the name iridium, from iris, the rainbow. The oxides are $Ir\,O$, $Ir_2\,O_3$, $Ir\,O_2$, and $Ir\,O_3$, and the chlorides correspond to them.

53. Osmium. $Os = 99{\cdot}72$.

This metal is found associated with iridium, constituting a small part of the ore of platinum, which is insoluble in aqua regia. When this residue is acted on at a red-heat, by nitre, both the metals are oxidised, and the mass being distilled with sulphuric acid, yields osmic acid, $Os\,O_4$, which condenses in fusible crystals. From the acid, the metal may be obtained by the action of reducing agents, as a black powder, which becomes metallic by friction.

Osmium is very infusible, and when it has been ignited in close vessels, may be heated in air without oxidation. It is chiefly remarkable for forming with oxygen a volatile acid, which has a pungent smell, like that of chlorine, and is very poisonous. It forms, altogether, 5 oxides, $Os\,O$, $Os_2\,O_3$, $Os\,O_2$, $Os\,O_3$ and $Os\,O_4$; 4 chlorides, and 4 sulphurets, corresponding to the 4 first oxides.

Klaus has lately discovered, in the residue of platinum ore, along with iridium and osmium, a new metal, which, from the red colour of its compounds, he calls ruthenium. It appears to be analogous to iridium, but has been hitherto little examined.

54. Palladium. $Pd = 53{\cdot}3$.

This metal is also one of those which occur in small quantity in the ore of platinum. It has lately been found rather more abundantly, alloyed with gold and silver. When the ore of platinum has been dissolved, and the solution rendered neutral by evaporation to dryness and resolution in water, a solution of bicyanide of mercury causes a flocculent, greyish-yellow precipitate of cyanide of palladium. When this is ignited, the palladium is left. It is rather more fusible than platinum, which it resembles in colour, lustre, and malleability, but is rather harder. Its Sp. G. is 11·3 to 11·8. From its not tarnishing, it is a valuable metal, and would be applied to many useful purposes, if it were less scarce. It is chiefly used by dentists in plates, as a substitute for gold. It is dissolved by nitric acid, but more easily by aqua regia.

Palladium forms two oxides: the protoxide $Pd\,O$, and the binoxide, $Pd\,O_2$, both of which are black when anhydrous, and brown or yellow when hydrated. The binoxide forms fine red salts, with acids, from which the palladium is precipitated, as metal, by other metals, and by deoxidising agents in general.

There are two corresponding chlorides, a black protochloride, $Pd\,Cl$, and a dark brown bichloride, $Pd\,Cl_2$. The former yields with chloride of potassium a yellow double chloride, the latter a red one.

The protosulphuret of palladium, $Pd\,S$, is easily formed by heating the metal with sulphur. It is a brittle fusible grey solid.

55. RHODIUM. $R = 52{\cdot}2$.

This metal is also found, in small proportion, in the ore of platinum. It is separated from platinum, when both are in the state of chloride, by adding chloride of sodium, with which both the chlorides form double salts, of which the platinum salt is soluble, the rhodium salt insoluble, in alcohol. When purified, the rhodium salt is dissolved in water, and the rhodium precipitated by metallic zinc. It appears as a black powder, which may be fused in a powerful wind furnace, and is then white and metallic, very hard, brittle, and of Sp. G. 11.

Rhodium is hardly dissolved by any acids, unless when alloyed with other metals. The best method of dissolving it is to fuse it with bisulphate of potash, when it forms a soluble double salt. Rhodium, from its great hardness, has been used to form the tips of metallic pens, which are said to last wonderfully.

It forms two oxides; a protoxide, and a sesquioxide, $R_2\,O_3$; and probably two corresponding chlorides. The solution of the sesquichloride is of a fine red colour, and most of the salts of rhodium are either red or yellow.

The sulphuret of rhodium is bluish-grey, metallic, and fusible at a white-heat.

ALLOYS.

The compounds of metals with metals are called alloys, and many of them are extremely useful and important. The alloys into which mercury enters, as a component part, are called amalgams.

Fine solder is an alloy of two parts of tin and one of lead. It melts at 360°. Coarse solder, which melts at 500°, contains one part of tin and three of lead. Hard solder, for copper, is a compound of copper and zinc, the latter metal being in excess.

Pewter is composed of tin, with a little antimony, copper, and bismuth ; the inferior kinds contain a good deal of lead.

Newton's fusible metal is composed of 8 parts of bismuth, 5 of lead, and 3 of tin. It melts below 212°.

Type metal is an alloy of 3 parts of lead, and 1 of antimony.

Bronze is composed of about 90 parts of copper to 10 of tin ; bell-metal and gong-metal, of 80 parts of copper to 20 of tin. Speculum metal, for telescopes, is formed of 2 parts of copper and 1 of tin, with a little arsenic.

Brass is an alloy of copper and zinc ; the best contains 4 parts of copper and 1 of zinc ; and when the proportion of zinc is increased, we have tombac, Dutch gold, and pinchbeck.

Tutenague, or white copper, as it is called in China, or German silver, as it is now called in Europe, is an alloy of copper, zinc, and nickel ; the finer kinds containing most nickel.

Steel appears to form valuable alloys with a very small proportion of some other metals. With a little silicon and aluminum, it yields a metal equal to the Indianwootz ; and with small quantities of silver, platinum, rhodium, palladium, and even iridium and osmium, alloys of prodigious hardness and toughness are obtained. $\frac{1}{500}$ part of silver is sufficient to effect a marked improvement.

Standard silver, and standard gold, are alloys, with from $\frac{1}{13}$ to $\frac{1}{12}$ of copper, which much increases the hardness of these metals, without injuring their colour.

An amalgam of tin is used for silvering the backs of mirrors ; and an amalgam of 4 of mercury, 2 of bismuth, 1 of lead, and 1 of tin, is used for silvering the inside of hollow glass globes.

The amalgam used for exciting electrical machines is formed of 1 part of zinc, 1 of tin, and 2 of mercury.

The tendency of mercury to combine with gold and silver is made use of in extracting these metals from their ores. An amalgam of 1 part of gold, and 8 of mercury, is used in gilding brass.

It is probable that the best alloys are those which contain atomic proportions of their ingredients; but this subject has been as yet little studied. Alloys are always more fusible than their least fusible ingredient, and they are commonly harder and more brittle than their elements. They are sometimes more dense, sometimes less dense than we should expect from the densities of the combining metals.

SALTS.

The salts are a very important and useful class of compounds; but our space will not allow us to describe them minutely, and we must be satisfied with a few general remarks, applicable to the whole class, and with a brief statement of the characters which distinguish the separate families of salts, as marked by the acids they contain. We have already given, under the different metals, the characters of the different bases in their salts. Fortunately the analogies among the very numerous salts are so strong and well marked, that here, better than in any other department, minute details may be omitted.

When the term salt was first extended beyond sea-salt, the original type, it was applied to substances having similar properties, such as solubility, neutrality, and saline taste, with the property of crystallising. It was found, after a time, that salts were produced by the combination of acids with alkalies, or at least by bringing them together; and as sea-salt was obtained when soda and muriatic acid were mixed, it was supposed to be formed of these constituents, just as sulphate of soda was supposed to consist of sulphuric acid and soda.

But when, in process of time, it came to be known that sea-salt contained neither muriatic acid nor soda, it was found necessary, since it was impossible to deny the claim of sea-salt to rank as a salt, to admit two kinds or classes of neutral salts, one formed of an oxygen acid and an oxygen base; the other, of a salt-radical and a metal. Thus, while sulphate of soda was $Na\,O, S\,O_3$, sea-salt was $Na\,Cl$; the former corresponding to the hydrated acid, $H\,O, S\,O_3$; the latter to the hydrogen acid, $H\,Cl$. This, indeed, is the view which has for many years prevailed.

But it did not escape the sagacious mind of Davy, that, according to this view, we give two different explanations of phenomena almost identical, and that a more truly philosophical view might be taken.

When hydrated sulphuric acid acts on soda, we have two marked phenomena: these are, the formation of a neutral salt and the separation of water. This is represented as follows: $Na\,O + H\,O, S\,O_3 = H\,O + Na\,O, S\,O_3$. Now, when hydrochloric acid acts on soda, we observe exactly the same phenomena—the formation of a neutral salt, and the separation of water; but the explanation is now different. It is $Na\,O + H\,Cl = Na\,Cl + H\,O$.

Davy showed that, in the latter case, but one explanation was possible—because the hydrogen could only come from the hydrochloric acid, and the oxygen from the soda; and he proposed so to view the former case as to bring it under the same explanation.

He pointed out that we have no certainty that the hydrated sulphuric acid really contains water; or the sulphate of soda, oxide of sodium; and that, instead of the formula $H\,O, S\,O_3$, we might with better reason adopt the formula $H, S\,O_4$ for the acid, which would thus come to be considered a hydrogen acid, differing from hydrochloric acid only in containing a *compound* radical, $S\,O$,, instead of a *simple* one, Cl. But, in the first place, chlorine may not be really a simple body; and secondly, if it were so, we know that compound radicals exist, performing exactly the part which is here ascribed to the hypothetical body $S\,O_4$.

Thus, cyanogen, $Cy = C_2\,N$, with hydrogen forms hydrocyanic acid, H Cy, which acts on bases exactly as hydrochloric acid does, yielding a neutral salt (a cyanide) and water. $M\,O + H\,Cy = M\,Cy + H\,O$.

Let us represent $S\,O_4$ by Su, and then we have H Su = hydrated or real sulphuric acid; and when it acts on soda, $Na\,O + H\,Su = Na\,Su + H\,O$. We have then—

	Chlorine.	Cyanogen.	Radical of Sulphuric Acid.
Radical . .	Cl . .	Cy . .	Su
Hydrogen Acid .	H Cl . .	H Cy . .	H Su
Neutral Salt . .	M Cl . .	M Cy . .	M Su.

In this form we see that, assuming sulphuric acid to be a hydrogen acid, the whole of its relations admit of being expressed as simply as those of hydrochloric acid. These two acids, and all acids analogous to either of them, come into the same category, and the same is true of their salts, all of which are considered compounds of metals with radicals, simple or compound. In this simple way we get rid of the absurdity of two different explanations for the same phenomena, and we arrive at the following general definition of an acid and of a salt:—

An acid is the hydrogen compound of a simple or compound radical, possessing the power of neutralising bases; and its general formula is $H\,R$.

A salt is the compound formed by replacing the hydrogen of an acid by a metal; and the general formula for a salt is $M\,R$.

This is the only view that can be taken in the case of the acids and salts of simple radicals; but in the case of compound radicals, we have already seen that another view is taken. For example, oil of vitriol is considered to be, not a hydrogen acid, but an oxygen acid united to water, and is called hydrated sulphuric acid, $H\,O, S\,O_3$; and in its salts the water is supposed to be replaced by metallic oxide, $M\,O, S\,O_3$.

In favour of this, the ordinary view, it is urged that dry sulphuric acid, $S\,O_3$, exists, and that, in contact with water, it produces hydrated sulphuric acid; in contact with bases, sulphates. That, although oil of vitriol may be viewed as H, SO_4, this view is improbable, because the body $S\,O_4$, the supposed radical, is unknown in a separate form, and that many undoubted oxygen acids exist containing no hydrogen, as carbonic, silicic, phosphoric, and chromic acids.

To these considerations it may be replied, that although the body $S\,O_3$ exists, it is not truly an acid, and does not acquire acid properties until it has been in contact with water, and combined with it, that is, with hydrogen. That with ammonia, $S\,O_3$ does not form sulphate of ammonia, but an entirely different compound. That, although the supposed radical $S\,O_4$ is unknown in a separate form, the same objection may be made to the older view in the case of nitric acid and many other acids; for strong nitric acid is viewed as a hydrate of dry nitric acid, $H\,O, N\,O_5$, while dry nitric acid is quite unknown in a separate form. That those oxygen acids which exist without hydrogen, such as dry sulphuric acid, $S\,O_3$, dry phosphoric acid, $P_2\,O_5$, carbonic acid, $C\,O_2$, silicic acid, $Si\,O_3$, and chromic acid, $Cr\,O_3$, either have no acid properties till water is added, as in the case of $S\,O_3$ and $P_2\,O_5$, or possess very feeble and ill-marked acid properties, as in the case of carbonic and silicic acids, which cannot neutralise the alkalies, and form with them an almost unlimited number of compounds. That all those oxygen acids which possess in perfection the acid character, such as oil of vitriol, nitric acid, phosphoric acid in its active state, and the whole of the organic acids, invariably contain hydrogen in a form in which it is replaced by metals in the salts, or, according to the older view, water, which in the salts is replaced by metallic oxide. Now, as in water, $H\,O$, and metallic oxide, $M\,O$, the oxygen is the same, it is, even on that view, hydrogen which is replaced by metal when an acid is converted into a salt.

It may be added, that considerations derived from the phenomena of galvanic decomposition (Daniell), from the heat developed when bodies combine to form salts (Graham, Andrews), and from the molecular or atomic volume of acids and salts (Kopp), all concur to render it probable that oxygen acids are hydrogen compounds, not hydrates, and that oxygen salts contain a metal united to a radical, and not an oxide united to a dry or anhydrous acid.

On the whole, therefore, the simpler view, and that which admits of but one kind of acids and one kind of salts, is, in the present state of our knowledge, to be preferred; but we shall give the formula according to both views, since we ought to be equally familiar with both.

Since salts are formed from acids by the replacement of the hydrogen of the acid by a metal, and since acids exist containing more than one equivalent of hydrogen (or of water) replaceable by metals (or metallic oxides), it is advisable to class the salts according to the acids from which they are derived, whether monobasic or polybasic.

SALTS OF MONOBASIC OXYGEN ACIDS.

Monobasic acids are those of which an equivalent forms a neutral salt with 1 eq. of base. The general formula of a monobasic acid, considered as a hydrogen acid, is HR, and its action on a protoxide is as follows: $HR + MO = HO + MR$; so that MR is the general formula for a monobasic salt. R stands here for the radical, which with hydrogen forms the acid.

On the other view, a monobasic oxygen acid is a hydrate containing 1 eq. of water and 1 eq. of dry or anhydrous acid, and the general formula is HO, RO_x; R standing here for the combustible element of any oxygen acid, which may be united with 2, 3, or more eq. of oxygen in the anhydrous acid. The action of such an acid on a base is as follows: $HO, RO_x + MO = MO, RO_x + HO$; so that, on this view, the general formula for a monobasic neutral salt is MO, RO_x.

The most important monobasic oxygen acids, of inorganic nature, are the following: sulphuric, sulphurous, nitric, hypochlorous, chloric, perchloric, iodic, phosphoric, arsenic, arsenious, chromic, boracic, silicic, and carbonic acids, the salts of which are now to be very briefly described. The salts formed by the monobasic hydrogen acids with simple radicals have been already described, under the respective metals, as chlorides, bromides, iodides, fluorides, sulphurets, &c.

SULPHATES.

General formula of neutral sulphates: M, SO_4, or MO, SO_3. General formula of bisulphates: $M, SO_4 + H, SO_4$; or $MO, SO_3 + HO, SO_3$.

Of the sulphates, some are found native; some are very soluble, some sparingly soluble, some insoluble. All the soluble sulphates are recognised in solution by the test of nitrate of baryta, which causes a white precipitate of sulphate of baryta, insoluble in acids. All the insoluble sulphates, when fused with carbonate of soda, yield sulphate of soda, which may be recognised as above; or, when heated with charcoal, they yield sulphurets, which are easily known by their blackening the salts of lead. The action of charcoal on a sulphate is thus represented: $MO, SO_3 + C_4 = 4\,CO + MS$; or $M, SO_4 + C_4 = 4\,CO + MS$.

The sulphates of the weaker bases are decomposed by a white heat, but those of the stronger bases are not altered.

Some neutral sulphates exist in the anhydrous state, MO, SO_3, or M, SO_4. Others occur combined with 1 eq. of what Graham calls constitutional water, requiring a red-heat for its expulsion, and capable of replacement by another neutral sulphate; and many occur with several equivalents of water of crystallisation.

Sulphate of potash crystallises in six-sided prisms and pyramids, which are anhydrous. Its formula is KO, SO_3, or K, SO_4.

Bisulphate of potash crystallises in fine needles, the formula of which is $(KO, SO_3 + HO, SO_3)$, or $(K, SO_4 + H, SO_4)$. It is a very acid salt, and is much used as a flux in mineral analysis.

Sulphate of soda, or Glauber's salt, forms large prisms, the formula of which is $Na\,O, SO_3 + 10\,aq.$; or $Na, SO_4 + 10\,aq.$ It is used as a laxative; and from this salt in its anhydrous state (prepared from sea-salt by the action of oil of vitriol), carbonate of soda is manufactured by heating it with charcoal in a reverberatory furnace.

Sulphate of ammonia (NH_3, HO, SO_3) or (NH_4, SO_4), crystallises in the same form as sulphate of potash. With water of crystallisation it forms crystals of a totally different form, $NH_4, O + SO_3 + aq.$

Sulphate of baryta, or heavy spar, occurs native in large tabular and also prismatic crystals. It is remarkable for its insolubility in water and acids. It is decomposed by ignition with charcoal, yielding sulphuret of barium, from which all the other compounds of barium may be obtained. It is anhydrous, and its formula is $Ba\,O, SO_3$, or Ba, SO_4.

Sulphate of strontia, or celestine, also occurs native, and is very analogous to the preceding. It serves, when decomposed by ignition with charcoal, to yield all the compounds of strontium. Formula $Sr\,O, SO_3$, or $Sr\,SO_4$.

Sulphate of lime. This salt occurs native, as gypsum, selenite, and alabaster, the formula of which is $(Ca\,O, SO_4 + HO) + aq.$; or $(Ca, SO_4 + HO) + aq.$ In the mineral anhydrite, it is anhydrous, $Ca\,O, SO_3$, or Ca, SO. When heated to 270°, gypsum loses both its constitutional water, and its water of crystallisation, and falls to a fine powder, which is plaster of Paris; and which, when mixed with water, combines with it again, forming a solid compound, or setting, as it is called. Hence its use in moulding. Gypsum is also a very valuable manure. It is very sparingly soluble in water, but its solution is precipitated copiously by salts of baryta.

Sulphate of magnesia, or Epsom salts, occurs in some springs, and is easily made by dissolving carbonate of magnesia in sulphuric acid. It is very soluble, and crystallises readily in four-sided prisms, the formula of which is $(Mg\,O, SO_3 + HO) + 6\,aq.$ It is much used as a laxative.

Sulphate of allumina does not crystallise, but it enters into the composition of crystallisable double salts, called alums. Its formula is $Al_2\,O_3, 3\,SO_3$, or $Al_2, 3\,SO_4$.

A subsulphate, or trisulphate of alumina, occurs native as the mineral aluminite. Formula $Al_2\,O_3, SO_3 + aq.$

Sulphate of manganese forms pale pink, or colourless crystals, of the formula $(Mn\,O, SO_3 + HO) + 4\,aq.$; or, $(Mn, SO_4 + HO) + 4\,aq.$

Sulphate of iron (protoxide) or green vitriol. This well-known salt forms pale-green oblique prisms. Formula $(Fe\,O, SO_3 + HO) + 5\,aq.$; or $(Fe, SO_4 + HO) + 5\,aq.$ It is used in the manufacture of fuming sulphuric acid, hence called oil of vitriol; in making ink; and very extensively in dyeing, and calico-printing. It is also much used in medicine.

Sulphate of the peroxide of iron does not crystallise, but forms crystallisable double salts. Formula $Fe_2\,O_3, 3\,SO_3$; or, $Fe_2, 3\,SO_4$.

Sulphate of zinc, or white vitriol, forms crystals exactly similar to those of sulphate of magnesia. Formula $(Zn, SO_3,$

$+ HO) + 6$ aq.; $(Zn, SO_4 + HO) + 6$ aq. It is much used in surgery, and is formed when zinc is dissolved in diluted sulphuric acid.

Sulphate of nickel forms emerald-green crystals, of the same form as the preceding. Formula $(Ni\,O, SO_3 + HO) + 6$ aq.; or $(Ni, SO_4 + HO) + 6$ aq.

Sulphate of cobalt forms rose-red crystals of the same form as green vitriol. Formula $(Co\,O, SO_3 + HO) + 5$ aq.; or, $(Co, SO_4 + HO) + 5$ aq.

Sulphate of chromium does not crystallise, but forms crystallisable double salts. Formula $Cr_2\,O_3, 3\,SO_3$; or, $Cr_2, 3\,SO_4$.

Sulphate of copper, or blue vitriol, forms azure-blue crystals, exactly of the same form as those of sulphate of manganese. Its formula is $(Cu\,O, SO_3 + HO) + 4$ aq.; or $(Cu, SO_4 + HO) + 4$ aq. With excess of ammonia it forms a deep violet-blue salt, the ammoniuret of copper, in which the water of crystallisation of blue vitriol, or a part of it, appears to be replaced by ammonia. Sulphate of copper is much used as an escharotic in surgery.

Sulphate of peroxide of mercury is formed as a crystalline powder, when mercury is boiled to dryness with sulphuric acid. Its formula is $Hg\,O_2, 2\,SO_3$, or $Hg, 2\,SO_4$. It is used in the preparation of corrosive sublimate, and of calomel.

Sulphate of silver forms anhydrous crystals, having the same form as those of anhydrous sulphate of soda. Formula $Ag\,O, SO_3$, or Ag, SO_4.

DOUBLE SULPHATES.

Of these there are two well-marked groups. The type of the first is sulphate of magnesia and potash; the type of the second is sulphate of alumina and potash, or alum.

1. When sulphate of potash and sulphate of magnesia are mixed in equivalent proportions, and the solution evaporated, crystals are deposited, of a well-marked form, the formula of which is $(KO, SO_3 + Mg\,O, SO_3) + 6$ aq.; or $(K, SO_4 + Mg, SO_4) + 6$ aq. It appears to have been formed from sulphate of magnesia, by the substitution of KO, SO_3, for the constitutional HO, the 6 aq. remaining unchanged. It is but the type of a large group; for similar double salts may be formed with sulphate of potash, and the sulphates of zinc, nickel, cobalt, iron, copper, and manganese; and another series, of exactly the same form, may be obtained by substituting sulphate of ammonia for sulphate of potash; as, for example,

in the double sulphate of magnesia and ammonia ($NH_4, O, SO_3 + Mg O, SO_3$) + 6 aq.

2. Common alum, the type of the second group, is formed when sulphate of potash combines with sulphate of alumina, and its formula is ($KO, SO_3 + Al_2 O_3, 3 SO_3$) + 24 aq.; or ($K, SO_4 + Al_2, 3 SO_4$) + 24 aq. Now, this is also the type of a numerous group; for the potash may be replaced by soda or ammonia, and the alumina may be replaced by the sesquioxides of iron, manganese, and chromium. The general formula of this group is ($MO, SO_3 + m_2 O_3, 3 SO_3$) + 24 aq.; M representing potassium, sodium, or ammonium, and m, aluminum, iron, manganese, or chromium. All the salts of this group, which are called alums, crystallise in octohedrons, and contain the same amount of water.

When we consider the facts above noticed, the circumstance that the sulphates of copper and manganese, with 4 eq. of water of crystallisation, those of iron and cobalt, with 5 eq., and those of magnesia, zinc, and nickel, with 6 eq. respectively crystallise in the same forms, different for each group; and when we reflect on the two remarkable groups of double sulphates just described, we cannot avoid the conclusion, that similarity of constitution is one main cause of similarity of crystalline form; and this constitutes the doctrine of isomorphism, as at present understood and admitted. By similarity of constitution is meant, not only a likeness in the nature of the elements present, but a similar arrangement of those elements.

Thus, in common alum, $K O, S O_3 + Al_2 O_3, 3 S O_3$ + 24 aq.; and in ammonia, iron, alum, $Am O, S O_3 + Fe_2 O_3, 3 S O_3$ + 24 aq.; not only is ammonium (Am) analogous to potassium, and iron to aluminum, but the new elements occupy the same position as the original ones, as is shown by the formula.

SULPHITES.

The sulphites are recognised by their giving off the suffocating smell of sulphurous acid when acted on by a stronger acid. They have lately been studied by Muspratt, who has found that a very close analogy exists between the sulphites and the carbonates.

NITRATES.

The nitrates are easily prepared by the action of nitric on bases, on metals, or on carbonates. They are all decomposed by a red-heat, and they all deflagrate with red-hot charcoal.

In solution, they are best recognised by adding sulphuric acid and warming, which sets free the nitric acid, and then cautiously adding solution of green vitriol, which, at the line of junction of the two liquids, becomes black or red, according to the proportion of nitric acid, from its peculiar action on the protosalts of iron. The general formula of nitrates, in the anhydrous state, is $M O, N O_5$, or M, NO_6.

Nitrate of potash, nitre or saltpetre, is found as an efflorescence on the soil in hot climates, and may be formed artificially in nitre beds. The essential conditions are the presence of a fixed base, particularly potash; and of decaying organic matter, or some other source of ammonia, which is oxidised, producing nitric acid and water; and the acid then unites with the base. The ammonia $N H_3$, with 8 eq. of oxygen from the air, gives rise to nitric acid and water, $N O_5 + 3 H O$, or $H, N O_6 + 2 H O$. There is no reason to believe that the nitrogen of the atmosphere is ever oxidised, or contributes to nitrification; and the minute trace of nitric acid sometimes observed in the rain of thunder-storms, has in all probability been formed from the ammonia of the atmosphere.

Nitre crystallises in 6-sided prisms. It is much used in making gunpowder, and as an oxidising agent; also in the manufacture of nitric acid. Formula, $K O, N O_5$, or $K, N O_6$.

Nitrate of soda is formed precisely in the same way, where soda is the base present in the soil, and occurs in immense quantities in some parts of South America. It crystallises in rhombohedrons. It is much used in the manufacture of sulphuric and nitric acids, but does not answer for gunpowder. Formula $Na O, N O_5$, or $Na, N O_6$.

Both nitre and nitrate of soda are used as manures: and it is still uncertain whether the acid of these salts contributes to the good effect, or whether they act by the bases alone.

Nitrate of ammonia crystallises in prisms like those of nitrate of potash. It is used in the preparation of the protoxide of nitrogen or laughing gas. Formula $N H_4 O, N O_5$ or $N H_4, N O_6$.

Nitrate of baryta crystallises in octohedrons, which are anhydrous. It is much used as a test, and when ignited yields pure baryta. Formula $Ba O, N O_5$, or $Ba, N O_6$.

Nitrate of strontia forms anhydrous crystals, isomorphous with the preceding salt; but it also occurs in large prismatic crystals, containing 5 eq. of water. It is used in the manufacture of red fire.

Nitrate of lime and nitrate of magnesia crystallise with difficulty, and are extremely deliquescent.

Nitrate of copper forms deep-blue crystals, the formula of which is $Cu\,O, N\,O_5 + 3\,H\,O$ or $Cu, N\,O_6 + 3\,H\,O$. There is also a subnitrate, the formula of which is $H\,O, N\,O_5 + 3\,Cu\,O$: the former salt may be viewed as nitrate of copper with 3 eq. of constitutional water, the latter as nitrate of water, with 3 eq. of constitutional oxide of copper. When either is ignited, it leaves pure oxide of copper, well adapted for organic analysis.

Nitrate of lead crystallises in octohedrons, and is isomorphous with the nitrates of baryta and strontia. Formula $Pb\,O, N\,O_5$ or $Pb, N\,O_6$.

Nitrate of mercury is of uncertain composition: there seem to be nitrates both of protoxide and peroxide, but both have a great tendency to form subsalts, especially in contact with water. When heated, the acid is driven off, and peroxide of mercury is left.

Nitrate of silver, or lunar caustic, is very much used as an escharotic. It is made by dissolving pure silver, or the oxide formed from the chloride (see p. 222) in nitric acid and evaporating, when crystals are deposited, which are fine tables, anhydrous, and fusible at 426°, when they may be run into a mould so as to yield the sticks of caustic. Formula $Ag\,O, N\,O_5$, or $Ag, N\,O_6$. It is the chief ingredient of indelible ink. Like all the other compounds of silver, it is blackened by light, especially when in contact with organic matter. It is much used as a test for chlorine.

CHLORATES.

The chlorates are, both in formula and properties, very analogous to the nitrates. They deflagrate violently with combustible matter, and are easily distinguished from nitrates by leaving chlorides when ignited. Their general formula is $M\,O, Cl\,O_5$, or $M, Cl\,O_6$.

The only important chlorate is chlorate of potash, the theory of the production of which has been already explained (see p. 77). It forms tabular crystals, of a pearly lustre. It is chiefly used as a convenient source of very pure oxygen gas, and as an oxidising agent. Its formula is $K\,O, Cl\,O_5$, or $K, Cl\,O_6$.

The perchlorate of potash, $K\,O, Cl\,O_7$, or $K, Cl\,O_8$, is the only perchlorate of interest. It is so sparingly soluble that perchloric acid may be used as a test for potash. It deflagrates with combustible matter, although not so powerfully as the chlorate.

HYPOCHLORITES.

These salts do not, in themselves, possess much importance, but are interesting as forming part of the bleaching compounds of lime and soda, so much used in the arts. These bleaching compounds, as explained at pp. 77 and 78, are formed when chlorine acts on an alkali or alkaline earth, and may be viewed either as composed of a hypochlorite and a chloride, or as oxychlorides of the metal. According to the former view, which is the more probable, bleaching-powder is $(Ca\,O, Cl\,O) + Ca\,Cl$. When acted on by an acid, the whole of its chlorine is set free, and hence its enormous bleaching power when an acid is used: hence, also, its want of bleaching power, unless acid is added. The action of sulphuric acid is as follows: $(Ca\,O, Cl\,O + Ca\,Cl) + 2\,S\,O_3 = 2\,(Ca\,O, S\,O_3) + Cl_2$. According to the latter view, bleaching powder is $Ca\,O\,Cl$, an oxychloride, and the action of sulphuric acid is $Ca\,O\,Cl + S\,O_3 = Ca\,O, S\,O_3 + Cl$.

Chloride of soda, a perfectly analogous compound, is either $Na\,O, Cl\,O + Na\,Cl$, or $Na\,O\,Cl$; and its action with sulphuric acid is explained exactly as above.

IODATES.

These salts are, in general, analogous to the chlorates, but are of little practical importance. The general formula for an iodate is $M\,O, I\,O_5$, or $M, I\,O_6$. When heated to redness, oxygen is given off, and an iodide remains.

The bromates are quite analogous to the chlorates. General formula, $M\,O, Br\,O_5$, or $M, Br\,O_6$.

PHOSPHATES.

There are three distinct modifications of phosphoric acid, each of which forms its own salts. Indeed, were it not that these acids, under certain circumstances, may be made to pass into each other, we should never think of describing them otherwise than as totally distinct acids. The three acids are, monobasic, bibasic, and tribasic phosphoric acids.

The so-called anhydrous phosphoric acid, formed by burning phosphorus in dry air or oxygen, is not, strictly speaking, an acid, and does not acquire acid properties till it has taken up the elements of at least 1 eq. of water, when it becomes monobasic phosphoric acid.

According to the usual view, the three acids are $P_2\,O_5, H\,O$, $P_2\,O_5, 2\,H\,O$, and $P_2\,O_5, 3\,H\,O$, thus containing, all of them, anhydrous acid united with different proportions of water. Now this is quite conceivable, and we actually possess three distinct hydrates of sulphuric acid, $SO_3\,HO$; $SO_3, 2\,HO$; and $SO_3, 3\,HO$. But we find, further, that the acid P_2O_5, HO requires but 1 eq. of base, to form a neutral salt, while the acid $P_2O_5, 2\,HO$ requires 2 eq.; and the acid, $P_2O_5, 3\,HO$, 3 eq. of base to form neutral salts. In the case of sulphuric acid the same phenomenon does not occur, for all the hydrates are neutralised by 1 eq. of base, yielding the same salt, and not, as the phosphoric acids do, different salts. What is the cause of this difference ? It is not enough to say that the dry acid, P_2O_5, being in the monobasic form combined with 1 eq. of water, has a tendency to take 1 eq. of base, and so on; for this is merely re-stating the fact in other words; and, besides, no such tendency is observed in sulphuric and in many other acids.

It appears to me that the only satisfactory answer to the question is the following. The three acids are all distinct acids, and none of them contains anhydrous phosphoric acid. They are all hydrogen acids; and their respective formulæ are P_2O_6, H; P_2O_7, H_2; and P_2O_8, H_3. Now as every hydrogen acid forms a neutral salt by the substitution of a metal for the hydrogen, these acids, if they exist, must require respectively, one, two, and three eq. of base to neutralise them, and must, of course, produce totally distinct salts: according to the equations, $P_2O_6, H + MO = P_2O_6, M + HO$; $P_2O_7, H_2 + 2\,MO = P_2O_7, M_2 + 2\,HO$; and $P_2O_8, H_3 + 3\,MO = P_2O_8, M_3 + 3\,HO$.

MONOBASIC PHOSPHATES.

According to the above views, therefore, the general formula for a monobasic phosphate is P_2O_6, M, or P_2O_5, MO. Monobasic phosphate of soda, P_2O_6, Na, or P_2O_5, NaO, is obtained by heating the acid tribasic phosphate of soda to redness, when it loses 2 eq. of water, and monobasic phosphate is left. It is soluble but not crystallisable, and gives, with chloride of barium, a bulky precipitate, which is P_2O_6, Ba, or P_2O_5, BaO; and with nitrate of silver, a flaky white precipitate, which is P_2O_6, Ag, or P_2O_5, AgO.

BIBASIC PHOSPHATES.

Of these there are two series, as one of the two eq. of base may be basic water, or both may be fixed base. The general formulæ for the two series are P_2O_7, M_2, or $P_2O\ $, $2\,MO$; and

$P_2O_7\left\{\begin{matrix}H\\M\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}HO.\\MO.\end{matrix}\right.$ Bibasic phospate of soda, P_2O_7, Na_2, or P_2O_5, $2\,NaO$, is obtained by exposing to a red-heat common tribasic phosphate of soda, which loses 1 eq. of water, and is converted into the new salt. It is soluble and crystallisable, and gives, with nitrate of silver, a granular white precipitate, which is P_2O_7, Ag_2, or P_2O_5, $2\,AgO$. When the acid tribasic phosphate of soda is heated to 400°, it loses 1 eq. of water, and leaves the acid bibasic phosphate, $P_2O_7\left\{\begin{matrix}H\\Na\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}HO.\\NaO.\end{matrix}\right.$

TRIBASIC PHOSPHATES.

Of these, which are the most usual phosphates, there are three series, the general formulæ for which are as follows: P_2O_8, M_3, or $P_2O_5, 3MO$: $P_2O_8\left\{\begin{matrix}H\\M_2\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}HO\\2MO\end{matrix}\right.$: and $P_2O_8\left\{\begin{matrix}H_2\\M\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}2\,HO.\\MO.\end{matrix}\right.$

Common phosphate of soda belongs to the second series: it is $P_2O_8\left\{\begin{matrix}H\\Na_2\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}HO\\2\,NaO\end{matrix}\right.$ when dry, to which, in the crystals, are added 24 eq. of water of crystallisation. By the addition of caustic soda, it is converted into P_2O_8, Na_3, or P_2O_5, $3\,NaO$; and by the addition of phosphoric acid, until it ceases to precipitate chloride of barium, it is converted into the acid tribasic salt, $P_2O_8\left\{\begin{matrix}H_2\\Na\end{matrix}\right.$ or $P_2O_5\left\{\begin{matrix}2\,HO.\\NaO.\end{matrix}\right.$ With nitrate of silver, either of these three salts yields a lemon-yellow precipitate, which is tribasic phosphate of silver, P_2O_8, Ag_3, or P_2O_5, $3\,AgO$.

Microcosmic salt, much used as a blow-pipe re-agent, is a tribasic phosphate, $P_2O_8\left\{\begin{matrix}H\\Na\\NH_4\end{matrix}\right. + 8\,aq.$ or $P_2O_5\left\{\begin{matrix}HO\\NaO + 8aq.\\NH_4O\end{matrix}\right.$ NH_4 here represents ammonium.

Bone phosphate of lime is a peculiar compound, $(8\,CaO + 3\,P_2O_5 + HO) = \left(P_2O_8\left\{\begin{matrix}H\\Ca_2\end{matrix}\right. + 2\,(P_2O_8, Ca_3)\right)$: or $P_2O_5\left\{\begin{matrix}HO\\2\,CaO\end{matrix}\right. + 2(P_2O_5, 3\,CaO)$; and may be viewed as a compound of two forms of tribasic phosphate of lime.

The double phosphate of ammonia and magnesia, which occurs in some urinary calculi, and is also found in the husk of grain and other vegetable products, appears to be an anomalous phosphate, containing (P_2O_5, 2 MgO, 2 NH_3, 10 HO), but how arranged is not known. This salt always separates as a sparingly soluble, or insoluble granular precipitate, when phosphoric acid, ammonia, and magnesia meet in neutral or alkaline solutions, and therefore its formation may be made a test, either of the presence of phosphoric acid, or of that of magnesia.

I have lately (see the process for preparing pure phosphoric acid from bones, page 115) obtained a new phosphate of magnesia. It is quite insoluble, and its formula is $3\,P_2O_5 + 2\,MgO$, or, adopting the higher atomic weight for phosphorus (see page 121), $3\,PO_5 + 2\,MgO$. This is a most remarkable composition, because it is quite anomalous, if we adopt the views above developed on the constitution of the phosphates. We cannot consider it as a monobasic, a bibasic, or a tribasic phosphate.

We may, it is true, adopting the older views regarding phosphoric acid, and rejecting all that we have learned concerning the three modifications of that acid, view it as an acid sesquiphosphate of magnesia. But it is easy to see that this view is quite irreconcilable with that which we must adopt regarding all other known phosphates. It is therefore possible, not to say probable, that this salt, being formed at a certain temperature, may contain a fourth modification of phosphoric acid; which will be $P_6O_{15}, 2\,HO$, when free, and the salts of which will be $P_6O_{15}, 2\,MO$ or $P_6O_{15} \left\{ \begin{matrix} MO. \\ HO. \end{matrix} \right.$ This point requires further investigation.

ARSENIATES.

The salts of arsenic acid are extremely analogous to those of tribasic phosphoric acid; indeed they are so similar, in form, colour, solubility, &c., that to distinguish the arseniate of a base from the corresponding tribasic phosphate, we must ascertain the presence of arsenic. The only case in which a well-marked difference in external properties exists, is in the case of the arseniate of silver, which, instead of being yellow, like the corresponding tribasic phosphate, is of a dark, brick-red colour. The arseniates are tribasic, and their general formulæ are, As_2O_8, M_3; or $As_2O_5, 3\,MO$: $As_2O_8 \left\{ \begin{matrix} H \\ M_2 \end{matrix} \right.$ or $As_2O_5 \left\{ \begin{matrix} HO \\ 2\,MO \end{matrix} \right.$ and $As_2O_8 \left\{ \begin{matrix} H_2 \\ M \end{matrix} \right.$ or $As_2O_5 \left\{ \begin{matrix} 2\,HO \\ MO \end{matrix} \right.$. Several arseniates are found native.

CHROMATES.

These salts are yellow, orange, or red, the latter colour predominating when the acid is in excess, except in the case of dichromate of lead, which is red. The soluble chromates are recognised by their colour, which is changed to green when alcohol and hydrochloric acid are added, and the mixture is boiled. The general formula for neutral chromates is $M\,O, Cr\,O_3$; and for bichromates, $M\,O, 2\,Cr\,O_3$.

Neutral chromate of potash, $K\,O, Cr\,O_3$, forms beautiful yellow crystals, isomorphous with sulphate of potash. It is formed by neutralising the bichromate with potash.

Bichromate of potash, $K\,O, 2\,Cr\,O_3$, is much used in calico-printing, and is obtained by fusing chrome iron ore with nitre. The ore contains sesquioxide of chromium, $Cr_2\,O_3$, which is oxidised by the nitre into chromic acid, $Cr_2\,O_6 = 2\,Cr\,O_3$, and this combines with the potash of the nitre to form neutral chromate. This is dissolved and filtered, and the warm solution acidulated with acetic acid, which takes half the potash, and, on cooling, the bichromate is deposited in beautiful red crystals.

Both these salts, especially the bichromate, have a very deleterious action on the system, when their solutions are brought much in contact with the skin, causing sores, which are very painful and difficult to heal. Paper impregnated with these salts, and dried, forms excellent tinder. The solutions have very powerful antiseptic properties.

Dichromate of lead, $2\,Pb\,O + Cr\,O_3$, is found native, as the red-lead ore, forming beautiful red crystals. It may also be formed by fusing the neutral chromate of lead with nitrate of potash, or by boiling carbonate of lead with chromate of potash; and is much used as a paint.

Chromate of lead, $Pb\,O, Cr\,O_3$, is an insoluble powder, of a very fine yellow colour, much used in painting, under the name of chrome yellow. It is formed by the action of soluble salts of lead on chromate, or bichromate of potash.

Chromate of silver, $Ag\,O, Cr\,O_3$, forms dark-green crystals, which are red by transmitted light, and yield a deep red powder. When precipitated, the salt is of a rich dark red.

Bichromate of silver forms crimson-red tabular crystals $Ag\,O, 2\,Cr\,O_3$. Chromate of mercury, $Ag\,O, Cr\,O_3$, is a light red powder, which, when ignited, leaves sesquioxide of chromium of a very fine green colour.

BORATES.

The only important borate is borax, which is a biborate of soda, $NaO, 2BO_3 + 10aq$. It is found native, but very impure, in Thibet, and is purified in Europe. It is also now formed by adding soda to the native boracic acid obtained from hot springs in Tuscany. Boracic acid is so feeble an acid that even the 2 eq. of it in borax do not fully neutralise the soda, so that borax is an alkaline salt. The borate of soda, with 1 eq. of acid, $NaO, BO_3 + 8aq.$, is a strongly alkaline salt.

Borax is much used as a flux, on account of its ready fusibility, and its high solvent power, at a red-heat.

CARBONATES.

These salts are recognised by their being decomposed with effervescence, the gas disengaged having no offensive smell, when acted on by acids. All the soluble carbonates, even those containing 2 eq. of acid to 1 of base, are alkaline, so that the title of carbonic acid to the name of acid is doubtful.

Carbonate of potash, KO, CO_2, is anhydrous, deliquescent, not crystallisable, insoluble in alcohol. It is obtained pure by igniting cream of tartar, and lixiviating the residue. In an impure state it constitutes pearlash and potashes, which are, as the name implies, the ashes of plants. Carbonate of potash is much used as a flux in mineral analysis, and for the preparation of caustic potash, and other salts of potash; also in the manufacture of soap, and of glass.

Bicarbonate of potash, $KO\ CO_2 + 2aq.$, is obtained by exposing a strong solution of the carbonate to a current of carbonic acid, or to the atmosphere of a fermenting vat, when the bicarbonate is deposited in crystals. The purest carbonate is obtained by igniting these crystals.

Carbonate of soda, $NaO, CO_2 + 10aq.$, forms very large rhomboidal crystals, which effloresce in the air. It was formerly extracted from kelp or barilla, which is the ashes of marine plants; but is now made from sea-salt, far more cheaply, and in a state of perfect purity. The salt, $NaCl$, is first converted into sulphate of soda, NaO, SO_3, by being heated with oil of vitriol. The sulphate of soda is now mixed with sawdust and lime, and heated in a reverberatory furnace. By this means the sulphuric acid is decomposed, its sulphur partly uniting with calcium, and partly escaping as sulphurous acid, while the carbonic acid which is formed unites with soda. The carbonate is purified by crystallisation, but generally retains a trace of sulphuric acid.

Carbonate of soda is very much used in the making of soap and glass, being both much cheaper and much purer than ordinary potash. It is also much employed by washerwomen to render hard water soft, and in general to assist in washing, as it is powerfully detergent.

Bicarbonate of soda, $NaO, 2 CO_2 + aq.$, forms a white powder, which is alkaline, and is much used in medicine as a mild antacid, and as one of the ingredients in effervescing or Seidlitz powders.

The common commercial and medicinal carbonate of ammonia is a sesquicarbonate, $2 NH_3 + 2 HO + 3 CO_2$. It is formed by heating a mixture of 2 parts of sal ammoniac and 3 of dried chalk, and sublimes as a hard crystalline volatile mass, having a strong smell of ammonia. When exposed to air, it loses ammonia, and falls to a powder of bicarbonate, $NH_4 O, CO_2 + HO, CO_2$.

Carbonate of baryta occurs native, as witherite. It forms, when artificially prepared, a heavy white powder, soluble in diluted hydrochloric and nitric acids, insoluble in water. It is very poisonous. Formula, BaO, CO_2.

Carbonate of strontia resembles the preceding. It occurs native, as strontianite, in radiated crystalline masses of an apple-green colour. It is not poisonous. Formula SrO, CO_2.

Carbonate of lime occurs native, as marble, limestone, chalk, and calcareous spar. It also forms the chief part of shells, and is often found in springs, dissolved by an excess of carbonic acid. When such water, which is very hard water, is boiled, the excess of carbonic acid escapes, the carbonate of lime is deposited, and the water becomes, *pro tanto*, softer. Or, the same effect may be produced by adding just as much lime-water as will neutralise the bicarbonate of lime, when the whole is precipitated as neutral carbonate. $CaO, 2 CO_2 + CaO = 2 (CaO, CO_2)$.

When carbonate of lime is ignited in the open fire, it loses all its carbonic acid and becomes quicklime. The uses of this substance are well known. Formula of carbonate of lime CaO, CO_2.

Carbonate of magnesia, MgO, CO_2, occurs as a rock in the East Indies. When a solution of bicarbonate is exposed to the air, crystals are deposited, which are $MgO, CO_2 + 3 aq$. Other crystals have been obtained, which were $Mg, O, CO_2 + 5 aq$. When carbonate of potash is added to a solution of sulphate of magnesia, a precipitate falls, which contains $4 MgO + 3 CO_2 + 4 aq$.

Carbonate of protoxide of iron is formed when an alkaline carbonate is added to a solution of protosulphate of iron. It falls as a dirty white bulky precipitate, which rapidly becomes green, and then brown, losing carbonic acid, and attracting oxygen, till it passes into hydrated peroxide of iron. It may be preserved as protocarbonate by mixing the fresh precipitate while still moist with sugar, and drying it in the water bath. In this state it is the carbonas ferri saccharatus, and is a very active remedy. It occurs in chalybeate waters, dissolved by excess of carbonic acid. Formula $Fe\,O, C\,O_2 + aq$.

There are two native carbonates of copper: the dicarbonate, $2\,Cu\,O + C\,O_2 + aq.$ in the beautiful green mineral called malachite; and the carbonate, hydrated, in the fine blue copper ore, $Cu\,O, H\,O + 2\,(Cu\,O, C\,O_2)$.

Carbonate of lead, $Pb\,O, C\,O_2$, occurs native as white lead spar. Prepared artificially, it is ceruse, or white lead, much used as a white pigment. It is formed by the slow action of air, moisture, and the vapour of acetic acid on thin sheets of lead, by which the metal is oxidised and carbonated. It is the most poisonous of all the compounds of lead, and is apt to be formed when pure water (as rain water) is kept in leaden cisterns or conveyed in leaden pipes. It is not formed, however, when the water contains even a small proportion of saline matter, especially sulphates. These appear to protect the metal, and render the use of it safe.

SULPHUR SALTS.

Berzelius has shown that sulphurets unite together, and produce what he calls sulphur salts. The sulphurets of potassium, sodium, and the strongly basic metals in general, act the part of bases; and the sulphurets of arsenic, antimony, molybdenum, &c., take the parts of acids. Thus sesquisulphuret of arsenic combines with sulphuret of potassium, forming the arsenio-sulphuret of potassium, $K\,S + As_2\,S_3$, which corresponds to the arsenite of potash, $K\,O + As_2\,O_3$; and as a general rule, the sulphur salts correspond to oxygen salts, and may of course be represented in two ways; as, if we make the arsenite of potash $K + As_2\,O_4$, the sulphur salt will be $K + As_2\,S_4$. The sulphurets of hydrogen and carbon are sulphur acids. The sulphur salts, as yet, are not of much practical interest, although the tendency to form them is applied to useful purposes in analysis.

Selenium and Tellurium form similar compounds.

END OF PART I.

OUTLINES OF CHEMISTRY.

PART II.

ORGANIC CHEMISTRY.

INTRODUCTORY.

ORGANIC CHEMISTRY is so called because it treats of the substances which form the structure of organised beings, and of their products, whether animal or vegetable. It has long been known, that all organised structures, as well as all the substances formed in or by these, are, in great part, composed of a very limited number of elements; insomuch that a large proportion of them may be described as consisting, almost exclusively, of only four simple substances, namely, Carbon, Hydrogen, Oxygen, and Nitrogen.

But while these four elements undoubtedly constitute the chief part of all organised tissues, and while such products as woody fibre, sugar, starch, gum, fat, oils, and many organic acids, contain only the first three, that is, Carbon, Hydrogen, and Oxygen, we must not forget that other elements occur in the organised kingdoms of nature; some of them, such as those of Phosphate of Lime, in large quantity; and all, whether they occur in smaller or greater proportion, as truly essential to animal and vegetable life, as the four elements above mentioned, the predominance of which characterises the organic world.

Thus, no plant can grow, or form cells, or even fibre, without the presence of certain mineral or saline compounds, which are derived from the soil, and which when the plant is burned, constitute its ashes. These are, Potash, Soda, Lime, Magnesia, with, occasionally, oxides of Iron and Manganese, as bases; and Silicic Acid, Phosphoric Acid, Sulphuric Acid, Chlorine and Fluorine, as acids and acid-radicals.

Again, the juices of all plants, and more especially their roots and seeds, contain some one or more of the compounds known by the names of albumen, fibrine, and caseine. Now these compounds contain small, but absolutely essential proportions of sulphur and phosphorus, besides earthy and alkaline phosphates.

Lastly, the bones of animals contain not only phosphate of lime, but also phosphate of magnesia and fluoride of calcium, both in very considerable quantity; and Iron is an unfailing constituent of blood.

To the four elements first mentioned, as constituting the chief mass of organic substances, we must therefore add, as no less essential, although for the most part in smaller proportion, the following metalloids, Chlorine, Fluorine, Sulphur, Phosphorus, and Silicon; and the following metals, Potassium, Sodium, Calcium, Magnesium, Iron, and occasionally Manganese.

It thus appears that the fourteen or fifteen elements which constitute the chief mass of the mineral or inorganic world, are almost the same which occur in organised matter: the difference being chiefly this, that in inorganic nature the *predominant* elements, nearly in the order of their abundance, are, Oxygen, Hydrogen, Nitrogen, Silicon, Chlorine, Sodium, Aluminum, Carbon, and Iron, after which follow Potassium, Calcium, Magnesium, Sulphur, Phosphorus, and Fluorine; while in the organic department the order is nearly as follows: Carbon, Oxygen, Hydrogen, Nitrogen, Potassium, Calcium, Phosphorus, Silicon, Sulphur, Sodium, Magnesium, Chlorine, Iron, and Fluorine. Aluminum, so very abundant in the mineral kingdom, hardly ever occurs in organic compounds, and when it does occur, is perhaps accidental.

The above considerations are sufficient to show, that there is no essential distinction to be made between organic and inorganic Chemistry, founded on the nature of the elements concerned.

Neither is there any such distinction to be pointed out in regard to the laws of combination and decomposition which prevail in these different departments of chemistry; for we find the same affinities operating; and although organised tissues, and their products, have, in general, a more complicated constitution than inorganic compounds, containing a larger number of equivalents of their elements, and consequently having much higher atomic weights, we cannot consider such characters as forming a valid ground of distinction.

But while we should find it very difficult, if not impossible, to draw the line between inorganic and organic Chemistry on scientific principles, we may still recognise, for convenience sake, a certain distinction, founded, first, on the origin of substances, whether animal and vegetable, or mineral; and secondly, on the uniform predominance of carbon in animal and vegetable matter.

In reference to the first point, it is to be observed, that, although the elements concerned are those common to the inorganic and organic kingdoms, the compounds which constitute the latter are formed under peculiar circumstances, such as, for the most part, cannot be imitated in our experiments.

It is true that chemistry has succeeded, in some cases, in forming artificially certain compounds which occur as products of organic life, such as Urea, Formic Acid, and Oil of Spiræa. But, in the first place, most, if not all of these, require for their production the aid of an organic product: thus, Formic Acid is produced from Starch, Oil of Spiræa from Salicine; and although Urea may be obtained from Cyanic Acid and Ammonia, it is doubtful if either Cyanogen or Ammonia can be obtained except from organic compounds, directly or indirectly. Secondly, it is particularly to be noticed, that we have not yet succeeded in forming, artificially, either an organised tissue, or even any one of the compounds (albumen, &c.) of which such tissues are made. Those organic compounds which have been artificially formed, are invariably *products of decomposition*, or, in other words, the excretions or secretions of organised bodies: and are far less complex in their constitution than organised structures.

From these facts we draw the conclusion, that certain circumstances, of which the most important is the *vital force*, so modify the play of affinities in organised beings, as to produce the compounds usually termed organic, which, so far as they are capable of entering into the composition of tissues, cannot be imitated by art.

In regard to the second peculiarity of organic compounds, namely, the predominance of carbon in their composition, we observe that, as this carbon is united to the three gases, Oxygen, Hydrogen, and Nitrogen, with each of which it forms gaseous compounds, and as, further, the latter elements, among themselves, form compounds, such as water and ammonia, which are also volatile, so the action of heat on organic compounds is characteristic; producing *combustion* of all, save the ashes, when there is free access of air; and *charring* them, or, in other words, causing the separation of part of their carbon, in close vessels, while the greater part is dissipated in the form of volatile products.

Here, then, we have a ready test of organic matter, which is so characteristic, that we might almost define Organic

Chemistry as the Chemistry of such compounds as are charred when heated to redness in close vessels. There are very few substances, indeed, of organic origin, which do not exhibit this character.

Organic Chemistry has been defined as the Chemistry of Compound Radicals; but, although we must admit the existence of many such radicals in Organic Chemistry, we cannot adopt this definition in contradistinction to that of Inorganic Chemistry, as the Chemistry of Simple Radicals, because the recent progress of science has led, or almost compelled us to admit the existence of compound radicals in Inorganic Chemistry, as has been explained in the First Part of this work.

It is, perhaps, worth while to point out, that all the organic compound radicals hitherto established, or supposed to exist, are compounds of carbon, if we except amidogen (see p. 68), which contains only hydrogen and nitrogen.

It is also proper here to state, that, under the name of organic compounds, many substances are treated of which do not occur in nature, but which have been obtained by subjecting true organic products to various influences: to that, for example, of heat, as in what is called the destructive distillation, which yields such substances as naphtha, naphthaline, &c.; or to the action of chlorine or bromine, of sulphuric or nitric acids, of alkalies, &c., by all which means whole series of new compounds are obtained. Lastly, some very interesting and important compounds are included under the term organic, which arise from the addition of elements not naturally occurring in the organic kingdom; as for example, kakodyle and its compounds, which contain arsenic as an essential constituent; and the very singular bases in which platinum is added to some of the usual elements of organic alkalies.

But while, as has just been stated, compound radicals are not exclusively characteristic of organic chemistry, we may still derive great assistance from attending to the compound radicals of organic chemistry. For while we admit the existence of such radicals in inorganic chemistry, along with simple radicals, we must bear in mind that all the organic radicals as yet discovered are compound, and many of them exceedingly complex, containing three or four elements.

It is true that we are not yet acquainted with the radicals of a very large proportion of organic compounds; such as the principal organic acids, the organic alkalies, &c. But the known organic radicals furnish us with the means of classifying many most important substances, just as we classify the compounds of any metalloid or of any metal together. As to those groups or series of organic compounds, the radicals of which are not yet known, we can only class them according to analogies of properties, of composition, or of both.

With these introductory remarks, we shall proceed to consider the known organic compound radicals, and their derivatives.

COMPOUND ORGANIC RADICALS.

A compound radical is a substance which, although containing two or more elements, enters into combination with elementary bodies as if it were itself elementary, and in ordinary circumstances performs exactly the part of an element.

In the First Part of this work, we have already admitted as probable the existence of inorganic compound radicals, such as SO_4, the radical of sulphuric acid, and NO_6, that of nitric acid. These bodies are, in their relations to others, entirely analogous to chlorine. Thus we may represent the acids of these three radicals, with their potassium and silver salts as follows :—

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine	$H + Cl$	$K + Cl$	$Ag + Cl$
	$S\,O_4$	$H + S\,O_4$	$K + S\,O_4$	$Ag + S\,O_4$
	$N\,O_6$	$H + N\,O_6$	$K + N\,O_6$	$Ag + N\,O_6$

The compound inorganic radicals, SO_4 and NO_6, therefore, perform exactly the part of a metalloid of the group of chlorine.

But there have also been briefly mentioned, in the First Part, certain compound organic radicals, which not only exhibit, in their relations, characters analogous to those of chlorine, but actually exist, like chlorine, in the separate state, which is not the case with SO_4 and NO_6, these latter being only known in combination.

The organic radicals here alluded to are Cyanogen, $C_2\,N =$ Cy, and Mellone $C_6\,N_4 =$ Me (see Part I., p. 128). They may be compared to chlorine exactly like the two above-mentioned inorganic compound radicals. Thus,

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine Cl	H + Cl	K + Cl	Ag + Cl
	Cyanogen Cy	H + Cy	K + Cy	Ag + Cy
	Mellone Me	H + Me	K + Me	Ag + Me

Cyanogen and Mellone are, therefore, radicals of the nature of the chlorine group of metalloids. The bisulphuret of cyanogen, or sulphocyanogen, $C_2\,N\,S_2 = Cy\,S_2$, although it contains three elements, plays the same part as chlorine or cyanogen, and forms with hydrogen the acid $H + Cy\,S_2$, with potassium the salt $K + Cy\,S_2$, and with silver the salt $Ag + Cy\,S_2$.

Some compound organic radicals appear more analogous to the combustible group of metalloids, that is, to carbon, sulphur, or phosphorus; inasmuch as they form acids with oxygen, or rather with the elements of water like those metalloids, and are besides capable of entering into combination with chlorine, iodine, &c. Such radicals are carbonic oxide, $C\,O$, or rather an isomeric modification of it, $C_2\,O_2$; acetyle, $C_4\,H_3$; and formyle, $C_2\,H$. Each of these may be viewed as the radical of a powerful acid; for $C_2\,O_2 + O = C_2\,O_3$ is dry oxalic acid; $C_4\,H_3 + O_3$ is dry acetic acid; and $C_2\,H + O_3$ is dry formic acid. Again, the first forms with chlorine the compound $C_2\,O_2 + Cl_2$, called phosgene gas or chlorocarbonic acid, while the two others yield $C_4\,H_3 + Cl$, the chloride of acetyle, and $C_2\,H + Cl_3$, the perchloride of formyle.

Further, there are organic compound radicals which play the part of metals, forming salts with chlorine, iodine, sulphur, cyanogen, &c., and yielding, with oxygen, compounds possessing basic properties analogous to those of metallic oxides. Such radicals are ethyle, $C_4\,H_5$, methyle, $C_2\,H_3$, and kakodyle, $C_4\,H_6\,As_2$.

Radicals.	Oxygen Compound.	Chlorine Compound.	Cyanogen Compound.	Sulphur Compound.
Ethyle $C_4\,H_5 = Ae$	$Ae\,O$	$Ae\,Cl$	$Ae\,Cy$	$Ae\,S$
Methyle $C_2\,H_3 = Mt$	$Mt\,O$	$Mt\,Cl$	$Mt\,Cy$	$Mt\,S$
Kakodyle $C_4\,H_6\,As_2 = Kd$	$Kd\,O$	$Kd\,Cl$	$Kd\,Cy$	$Kd\,S$

Lastly, there are some compound organic radicals, which partake of the characters of the two last groups, forming, like the acetyle group, acids and not bases with oxygen; but yielding, with chlorine, sulphur, cyanogen, &c., compounds analogous to those formed by the ethyle group. To this division belong Benzoyle, $C_{14}\,H_5\,O_2 = Bz$; Cinnamyle, $C_{18}\,H_8\,O_2 = Ci$; and several others. Benzoyle and cinnamyle, with the addition of oxygen and the elements of water, produce benzoic acid, $Bz\,O,\ HO$, and cinnamic acid, $Ci\,O,\ HO$. This group is characterised by forming with hydrogen certain essential oils.

Thus, benzoyle yields, with hydrogen, the essential oil of bitter almonds, Bz H ; cinnamyle yields the oil of cinnamon, Ci H ; and salicyle, $C_{14} H_5 O_4 = Sa$, another radical of this group, forms, with hydrogen, the oil of spiræa, Sa H.

These brief statements will serve to show that there are different kinds or groups of compound radicals, just as there are of simple ones ; and further, that these compound radicals exhibit a very remarkable tendency to combine with simple radicals, and, in fact, to act the part of elementary bodies. And let us here bear in mind that the only real difference, in this point of view, between cyanogen and chlorine is this, that in the case of the former we can prove the radical to be compound, while we cannot as yet do this in the case of the latter. But, as formerly pointed out, we call chlorine, and indeed all other elements simple, only because we have not been able to show them to be compound; without having any certainty that they are really and absolutely simple. If we could not resolve cyanogen into carbon and nitrogen, we should be compelled to add it to the list of elements.

But although compound radicals usually act towards other bodies as if simple, and consequently combine generally with simple substances, they are also capable of uniting with each other. In fact, this is but another proof of their close resemblance to elementary bodies in their relations ; for as simple metals, such as potassium and silver, unite with cyanogen just as with chlorine, so also such compound radicals as are analogous to metals can combine with cyanogen, itself a compound radical. Thus ethyle, methyle, benzoyle, and kakodyle all combine with cyanogen, yielding compounds formed of two organic radicals, one playing the part of a metalloid, the other that of a metal.

Compounds of this nature furnish the very best proof and illustration of the advantages which we derive from the doctrine of compound radicals, acting like elements, whenever we are justified by facts in adopting and applying it. Thus a compound has been formed by the mutual action of a compound of kakodyle and a compound of cyanogen, the analysis of which proves that it contains carbon, hydrogen, nitrogen, and arsenic, in the relative proportions indicated by the formula $C_6 H_6 N As_2$. What view are we to take of such a formula? and if we look on the compound as one formed of these four elements indiscriminately united, how are we to retain such an isolated fact in the memory? But if, on the other hand, we view it as the cyanide of kakodyle, $= C_4 H_6 As_2 + C_2 N$, or, using the abbreviated notation appropriate to compound radicals, Kd Cy, we are at once enabled to retain the composition and chemical relations of the compound. Moreover, when we find that the radical, Kd ($=C_4\ H_6\ As_2$) exists in a separate form, and that it forms, with oxygen, two compounds, Kd O and $Kd\ O_3$; with chlorine, Kd Cl; with sulphur, Kd S; and that, in short, it plays the part of a metal in all its compounds, and may in fact be separated from some of these by metals having stronger affinities than itself, we are supplied with an idea which serves to connect and to fix all these and many more analogous facts in the memory.

When we further observe, to pursue the same example, that the cyanide of kakodyle, Kd Cy, when acted on by hydrochloric acid, gives rise to hydrocyanic acid and chloride of kakodyle; and that, when acted on by potash, it yields cyanide of potassium and oxide of kakodyle, we acquire so many additional proofs of the entire analogy between simple and compound radicals in their relations to other bodies. For the two changes or reactions above mentioned are expressed by the equations, $Kd\ Cy + H\ Cl = Kd\ Cl + H\ Cy$; and $Kd\ Cy + K\ O = Kd\ O + K\ Cy$; and these equations are exactly similar to those which occur most frequently in inorganic chemistry.

The facts already ascertained with regard to those compound organic radicals, whose existence has been either established, or rendered highly probable, entitle us to conclude that all organic compounds contain one or more organic radicals, combined either with each other, or with elementary radicals. In studying, therefore, any organic product, one chief object is to determine what organic radical or radicals it contains, since the knowledge of these at once gives us a means of classification.

Thus alcohol, on the theory of compound radicals, is considered as the hydrated oxide of ethyle; ethyle being an organic radical, $C_4\ H_5$. So that alcohol, $C_4\ H_6\ O_2$ is more accurately represented as $(C_4\ H_5)\ O + H\ O$; or, if we represent ethyle, $C_4\ H_5$, by Ae, then alcohol becomes Ae O, H O, hydrated oxide of ethyle; perfectly analogous to K O, H O, hydrated oxide of potassium, or caustic potash.

Again, benzoic ether, $C_{18}\ H_{10}\ O_4$, is viewed as benzoate of oxide of ethyle, $C_4\ H_5\ O + C_{14}\ H_5\ O_3$; or, more briefly, $Ae\ O + Bz\ O$. Here we have the basic oxide of one radical united with the acid oxide of another.

It is often by means of thus tracing the different organic radicals, that we are enabled to explain the very numerous cases of isomerism, which occur in organic chemistry. Thus, the following compounds have the same composition in 100 parts:—

Aldehyde	$C_4 H_4 O_2$
Acetic Ether	$C_8 H_8 O_4$
Butyric Acid . . .	$C_8 H_8 O_4$

Now, aldehyde is considered to be the hydrated protoxide of acetyle, $(C_4 H_3) O + H O$; or, abbreviated, Ac O, H O. Again, acetic ether is acetate of oxide of ethyle, $C_4 H_5 O + (C_4 H_3) O_3$; or, shortly, Ae O, Ac O_3; the dry acetic acid, Ac $O_3 = (C_4 H_3) O_3$, being a peroxide of the same radical, acetyle, $(C_4 H_3 = \text{Ac})$ of which aldehyde is the protoxide. Lastly, butyric acid is considered (on the older view of acids,) as a hydrated acid, a compound of water with dry butyric acid; thus, $H O + C_8 H_7 O_3$. It is true, that, in the latter case, we are not yet acquainted with the true radical of butyric acid; but, we cannot doubt that, like acetic acid, it does contain a radical. These three compounds, therefore, may now be represented and distinguished as follows :—

	Empirical Formula.	Rational Formula.
Aldehyde . .	$C_4H_4O_2$	$= (C_4H_3)\ O + HO$
Acetic Ether .	$C_8H_8O_4$	$= (C_4H_5)\ O + (C_4\ H_3)O_3$
Butyric Acid .	$C_8H_8O_4$	$= C_8H_7O_3 + HO$

Even in those cases in which the composition of the radical is not known, or not known with certainty, we can often trace the radical with much probability. Thus, dry oxalic acid, $C_2\ O_3$, and dry mellitic acid, $C_4\ O_3$, may be viewed as different compounds of the simple radical carbon, the latter containing just twice the proportion of carbon to the same quantity of oxygen that the former does. This is merely stated by way of illustration: for, it is at least equally probable that the true radical of oxalic acid is $C_2\ O_2$.

But in the following four acids we may trace, theoretically, the same compound radical, namely, formyle, $= C_2\ H$, in combination with different proportions of oxygen. Here $C_2\ H$ is also represented by Fo.

Formic Acid	$(C_2H) + O_3 = \text{Fo}\ O_3$
Succinic Acid	$C_4H_2O_3 = 2\ (C_2H) + O_3 = \text{Fo}_2O_3$
Malic Acid	$C_4H_2O_4 = 2\ (C_2H) + O_4 = \text{Fo}_2O_4$
Racemic Acid	$C_4H_2O_5 = 2\ (C_2H) + O_5 = \text{Fo}_2O_5$

These relations, although as yet only to be traced in the formulæ, are yet not without interest, and may, at all events, serve to aid the memory.

In like manner, it may be observed, that the following acids all contain, as hydrates, 4 eq. of oxygen; and all likewise the same number of eqs. of carbon as of hydrogen.

1.	Acetic Acid	$C_4 H_4 O_4 = C_4 H_3 O_3, HO$
2.	Metacetonic Acid . . .	$C_6 H_6 O_4 = C_6 H_5 O_3, HO$
3.	Butyric Acid	$C_8 H_8 O_4 = C_8 H_7 O_3, HO$
4.	Valerianic Acid	$C_{10} H_{10} O_4 = C_{10} H_9 O_3, HO$
5.	Caproic Acid	$C_{12} H_{12} O_4 = C_{12} H_{11} O_3, HO$
6.	Œnanthylic Acid . . .	$C_{14} H_{14} O_4 = C_{14} H_{13} O_3, HO$
7.	Caprylic Acid	$C_{16} H_{16} O_4 = C_{16} H_{15} O_3, HO$
8.	Pelargonic Acid	$C_{18} H_{18} O_4 = C_{18} H_{17} O_3, HO$
9.	Capric Acid	$C_{20} H_{20} O_4 = C_{20} H_{19} O_3, HO$
10.	* * *	* * * * *
11.	Lauric Acid	$C_{24} H_{24} O_4 = C_{24} H_{23} O_3, HO$
12.	Cocinic Acid	$C_{26} H_{28} O_4 = C_{20} H_{25} O_3, HO$
13.	Myristic Acid	$C_{28} H_{28} O_4 = C_{28} H_{27} O_3, HO$
14.	* * *	* * * * *
15.	Palmitic and Ethalic Acids	$C_{32} H_{32} O_4 = C_{32} H_{31} O_3, HO$
16.	Margaric Acid	$C_{34} H_{34} O_4 = C_{34} H_{33} O_3, HO$

Here we may suppose the radical of the first acid to have been changed by the successive additions of 2, 4, 6, 10, or 20, or more eqs. of carbon and hydrogen, the oxygen remaining unchanged. Or we may as readily suppose one of these acids, by losing oxygen, to pass into another. Thus we may either conceive butyric acid to be formed from acetic acid by the addition of $C_4 H_4$; or acetic acid to give rise to butyric acid, by losing half its oxygen; for $2 (C_4 H_4 O_4) = C_8 H_8 O_8$; and $C_8 H_8 O_8 - O_4 = C_8 H_8 O_4$.

When compound organic radicals, or their compounds, are subjected to powerful decomposing agencies, they tend to produce new and less complex radicals. Thus, when alcohol, the hydrated oxide of ethyle, is oxidised, it gives rise to aldehyde and acetic acid, which are compounds of acetyle, $C_4 H_3$, a less complex radical than ethyle, $C_4 H_5$. Further, when organic compounds are decomposed by a strong heat, they tend to produce compounds of simple radicals, such as carbon or hydrogen, or, at most, of the least complex radicals, such as cyanogen, $C_2 N$, and amidogen, $N H_2$. These are principles of very general application.

It may here be observed, that while, in such cases as the supposed conversion of acetic into butyric acid, by the *loss* of half its oxygen, the change is from a less complex to a more complex organic compound, and while we can hardly doubt the possibility of such a result, yet the *oxidation* of a compound radical, that is, the addition of oxygen, appears always to produce less complex radicals or compounds.

It is often urged, as an argument against the doctrine of compound radicals, that these supposed radicals are entirely imaginary, and cannot be produced. Now, it is true, that a large proportion of those, whose existence is best attested, have not yet been obtained in the uncombined state ; and it is even probable that some of them are only capable of existing, or rather of being preserved, when combined. But the argument founded on this fact has no cogency ; for, in the first place, some organic radicals, such as cyanogen and kakodyle, are well known in the separate state. Now cyanogen and kakodyle are, in all their relations, exactly analogous, the former to chlorine, the latter to a metal ; and, if we were unable to demonstrate their compound nature, their chemical relations would compel us to classify cyanogen as an element along with chlorine, and kakodyle along with the metals ; and when we see whole series of organic compounds, in all respects analogous to those of cyanogen and kakodyle, we are entitled logically to draw the conclusion that these compounds contain similar compound radicals, even although we cannot isolate them. Secondly, in every chemical theory yet broached, many substances are admitted whose existence cannot be directly proved. Thus, the so-called anhydrous organic acids are, almost without exception, unknown in the separate state ; they are equally imaginary with the radicals whose existence is doubted. Nay, many inorganic acids are equally hypothetical. Anhydrous nitric acid has never been seen ; and, although there are reasons for doubting its existence, yet no one doubts the existence of hyposulphurous acid, which yet has never been separated, either as a hydrate, or in the anhydrous state.

We conclude, therefore, that organic compound radicals exist, and generally play the part of elements ; and we shall avail ourselves of their existence, as far as it is established, to facilitate the study, the classification, and the retention in the memory, of organic compounds.

THEORY OF CHEMICAL TYPES.—DOCTRINE OF SUBSTITUTION.

The original and ingenious researches of Laurent have led to the adoption of what is called the Theory of Types and the Law or Doctrine of Substitution, which have been supported, and in a great measure established, by Dumas and other distinguished experimenters of the French school. The views of Laurent and of Dumas were, for a time, vehemently opposed by some chemists, especially by Berzelius and Liebig; but although they have in some points been modified and restricted, the progress of discovery has gradually led to their general reception, so that recently some of the most striking illustrations and proofs of the law of substitution have been discovered by Dr. Hoffman, assistant to Baron Liebig, and working under his eye.

As the subject, therefore, is no longer purely controversial, it would be wrong to omit it in an elementary work, more especially as the doctrine has now taken such a form as to facilitate very much the study of organic compounds and of their metamorphoses.

It is not easy to define a chemical type; but in inorganic chemistry we may say, for example, that hydrochloric acid, $H\,Cl$, is the type of a very numerous class of acids, the character of which is that they contain hydrogen united to a salt radical.

If for chlorine we substitute iodine, bromine, &c., or even cyanogen, the type remains unchanged, the compound is still an acid, analogous to that which was selected as the type.

Again, common salt, $Na\,Cl$, is the type of a very large series of salts, in which a metal is united with a salt radical; and if we substitute potassium, lead, or silver for the sodium, the type is unaltered; we obtain a different salt, but still a salt of the type represented by $Na\,Cl$.

Here, then, we have the simplest types and the most obvious cases of substitution; when iodine or cyanogen is substituted for chlorine in the acid type; or when potassium, lead, or silver is substituted for sodium in the salt type; in both cases without the loss of the type.

Nay in the salt type, represented by $Na\,Cl$, we may not only replace sodium by other metals, but we may also substitute iodine, bromine, etc., or cyanogen for the chlorine, and still the type will remain unchanged. Iodide of sodium, $Na\,I$, bromide of magnesium, $Mg\,Br$ and cyanide of silver, $Ag\,Cy$, are all as good examples of the salt type represented by $Na\,Cl$, as common salt itself is.

It has been proposed, with great propriety, by Baudrimont, to employ certain Greek characters as symbols in representing the formulæ of extensive types or of types in general. I shall, therefore, express the above salt type by the formula ΔX, in which Δ stands for any metal or body acting as a metal, and X for chlorine or any other radical of analogous power, such as cyanogen. As hydrogen appears to stand alone in the power of forming acids with bodies of the type X, the acid type above alluded to becomes, in its most general form, HX.

But while it is very easy to understand the extensive substitutions which may be effected in the case of both elements of the type ΔX, yet we observe that in these substitutions the electrical character of the elements is retained; and that as Δ is the positive, and X is the negative element, so they are only replaced, Δ by positive and X by negative elements respectively.

So far as inorganic chemistry is concerned, the study of types would serve generally to confirm and establish the electro-chemical theory. At all events, we are not as yet acquainted with many exceptions to it; we do not usually find oxygen or chlorine occupying the place of Δ in a compound, or a metal playing the part of X. Even in inorganic chemistry, however, there are some examples of such interchanges. Manganese in manganic acid, $Mn\,O_3$, and chromium in chromic acid, $Cr\,O_3$, obviously represent the sulphur in sulphuric acid; and the manganese in hypermanganic acid, $Mn_2\,O_7$ represents the chlorine in perchloric acid, $Cl\,O_7$; while, in its other compounds, manganese acts as a metal.

But the researches of Laurent and Dumas have shown that in organic chemistry the substitution of one element for another, even where the type is retained, is not limited by the electrical character of the elements. Thus, in acetic acid, $H\,O, C_4\,H_3\,O_3$, the 3 eq. of hydrogen in the anhydrous acid may be replaced by chlorine, giving rise to the compound $H\,O, C_4\,Cl_3\,O_3$, in which the type is so little effected, that this substance, chloracetic acid, has properties highly analogous to those of acetic acid. Here it is evident that the chlorine performs the same function as the hydrogen which it replaces did; and not, as in hydrochloric acid, an opposite function.

Again, in aldehyde, $(C_4\,H_3)\,O + H\,O$, the 3 eq. of hydrogen in the radical C_4H_3 may be replaced by 3 eq. of chlorine, and we then have chloral, $(C_4\,Cl_3)\,O + H\,O$, a body of the same type as aldehyde.

Such cases of substitution of chlorine (iodine, bromine, &c.,) for hydrogen, and even of oxygen for hydrogen, without change of type, are very frequent; and it is this kind of substitution, so adverse to the electro-chemical theory, which is included in the theory of substitutions of Laurent. Those more usual substitutions, where one body is replaced by another of similar electric character, may be viewed as so many examples of the doctrine of equivalents, the replacing body being equivalent to that for which it is substituted, on the electro-chemical theory.

Adopting, then, the views of Laurent, we are compelled to admit that the electro-chemical theory fails when applied to cases of substitution of chlorine for hydrogen, &c., where the type remains unaltered. This is clearly the case in acetic and chloracetic acids; and Hoffman has recently shown that in certain basic organic compounds, hydrogen may be replaced by chlorine, while the new compound retains the basic type and characters. Aldehyde and chloral furnish an example of the same, in a body neither acid nor basic.

Here, then, is a fact of very general occurrence, which not only proves that the electro-chemical theory of combination is inapplicable, at all events in many cases, but also tends to establish a very different view: namely, that the electric character of an element is no permanent or essential property; and that the type or character, or general properties of a compound, depend, not on the *nature*, but solely on the *arrangement* of its elementary atoms; on the way in which they are grouped to form the compound molecule.

The reader will remember that, in the section on Isomorphism, the principle was laid down that the crystalline form of certain types of salts, such as the alum type, as well as many other properties of the compounds having those types, were the result of the *similar grouping* of *analogous elements.* We now see that, according to the law of substitution, as deduced from numerous careful observations, similarity of properties, or identity of type, are the result of similarity of grouping, even of elements not analogous, nay, of elements electrically opposed to each other. It is evident, therefore, that the arrangement of the elementary molecules to form the compound molecule is the circumstance on which depend almost exclusively the properties of the compound, or, in other words, the character of the type.

Substitution may be either complete or partial. In chloracetic acid, and in chloral, the substitution of chlorine for the hydrogen of the radical acetyle $C_4\,H_3$ is complete. But when ether $(C_4\,H_5)\,O$ is acted on by chlorine, the substitution takes place by successive steps, one equivalent of hydrogen being replaced at a time, after the oxygen has also been replaced by chlorine. Thus we have, first—

$$\begin{array}{rl}
\text{Ether or oxide of ethyle} = & (C_4H_5) + O \\
\text{then, chloride of ethyle} = & (C_4H_5) + Cl \\
\text{then, successively,} & C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right. + Cl \\
 & C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right. + Cl \\
 & C_4 \left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right. + Cl \\
 & C_4 \left\{\begin{matrix} H \\ Cl_4 \end{matrix}\right. + Cl \\
\text{and lastly,} & (C_4\,Cl_5) + Cl
\end{array}$$

We thus obtain the series of compounds here indicated, in which the hydrogen is gradually replaced by chlorine, until at last we obtain the compound $(C_4\,Cl_5) + Cl = C_4\,Cl_6 = 2\,C_2Cl_3$, which is the perchloride of carbon. Most of these compounds have actually been obtained; and it is obvious that they may all be referred to one type. Such a series is called a series of mechanical examples of the type in question, or rather of subtypes retaining the original character although modified.

In some cases, hydrogen has been replaced partly by chlorine, and partly by bromine. Laurent has described two compounds derived from naphthaline by substitution, the empirical formula for both of which is the following :—$C_{20}\ H_4\ Cl_3\ Br$. Yet the properties of these two compounds are quite distinct, and it is certain that this difference of properties must depend on a difference in the arrangement of the elements. Now, in the formation of these two compounds we have a very beautiful proof of the existence of a difference in the arrangement : for one is produced when chlorine acts on the compound called by Laurent bronaphtése, $C_{20}\ H_6\ Br_2$; while the other is formed when bromine is made to act on chlonaphtise, $C_{20}\ H_5\ Cl_3$. It is obvious that in the first case 2 eq. of hydrogen and 1 eq. of bromine are replaced by chlorine ; while in the second, 1 eq. of hydrogen is replaced by bromine. While, therefore, all four compounds may be deduced from the type $C_{20}\ H_8$, and while both the bromine and chlorine play the part of hydrogen, it is impossible to doubt that each of the 8 eq. of hydrogen has its special place in the compound molecule of the type, and that, in the two empirically identical formulæ above given, the 1 eq. of bromine does not replace the same eq. of hydrogen, and consequently the bromine occupies in the two compounds different positions. The same remark applies to the 3 eq. of chlorine.

We may illustrate our meaning as follows :—Let $C_{20}\ H_8$ be the type, and let each of the eqs. of hydrogen have a number attached indicating its place in the typical molecule. We shall then have

$$C_{20}\left\{\begin{matrix} H_1\ H_2\ H_3\ H_4 \\ H_5\ H_6\ H_7\ H_8 \end{matrix}\right\}$$

Now, if we represent the two compounds above mentioned in the following manner, we can then conceive the influence of arrangement on the properties of two compounds having the same empirical formula. The first may be

$$C_{20}\left\{\begin{matrix} H_1\ H_2\ H_3\ H_4 \\ Cl_5\ Cl_6\ Cl_7\ Br_8 \end{matrix}\right\}$$

and the second may be

$$C_{20}\left\{\begin{matrix} H_1\ H_2\ H_3\ Br_4 \\ Cl_5\ Cl_6\ Cl_7\ H_8 \end{matrix}\right\}$$

It is only on this principle that we can explain the facts observed by Laurent ; and it is easy to see that the above type, $C_{20} H_8$, will admit of innumerable modifications; for even the subtype, $C_{20} H_4 Cl_3 Br$. is capable of yielding many more than the two above given; and the change of 1 eq. produces a new subtype, equally fertile in new forms.

In fact, Laurent has actually obtained, as will be shown further on, a very large number of what we have called subtypes from the type $C_{20} H_8$, which is naphthaline, and has established the same law in reference to many other types.

The preceding observations will, I trust, be found sufficient to convey a clear general notion of the prevalent doctrines of chemical types and of substitution, as applied to organic chemistry. It is evident that the facts of substitution are of great interest, and not only enable us to classify and to remember numerous complex facts, but promise to throw much light on the molecular constitution of compound bodies. But while admitting the importance of the doctrine of substitution, it is necessary to point out that the French chemists appear to have gone too far in assuming that this doctrine is incompatible with that of compound radicals. It is certain that some compound radicals exist, and it is no less certain that by assuming their existence in other cases, we very much facilitate the study of many important series of compounds. Let us, therefore, avail ourselves of that which appears well founded in both doctrines, since there appears to be no reason why the one should be opposed to the other.

THE DECOMPOSITIONS AND METAMORPHOSES OF ORGANIC COMPOUNDS.

Organic compounds, whether actual organised tissues, unorganised products of animal and vegetable life, or new substances artificially produced, are generally characterised by a great proneness to undergo decomposition or metamorphosis. This instability is especially marked in those compounds which contain nitrogen, not only, because, containing four elements (in most cases), they are exposed to more numerous causes of change than such bodies as contain only three (carbon, hydrogen, and oxygen), but also because nitrogen is, in its relations to those three elements, the most remarkable element we know. According to the circumstances under which a change is induced, nitrogen may separate uncombined, as in the ultimate analysis of organic substances by combustion with oxide of copper or chromate of lead; or it may combine with oxygen, yielding nitric acid, as in nitrification; or with carbon, yielding the compound radical cyanogen, as when nitrogenised organic matter is ignited with carbonate of potash; or with hydrogen, yielding ammonia, as when nitrogenised organic matter is ignited with hydrated alkalies.

It is easy to see, therefore, that while all organic matter is prone to change, this is especially the case with nitrogenised compounds. In fact, many of these compounds cannot be kept more than a few hours without the commencement of decomposition or metamorphosis, in the shape of putrefaction or fermentation. This kind of metamorphosis will be separately considered hereafter; in the meantime it is important to observe, that when such a compound has entered into a state of decomposition, it acquires the properties of a ferment, that is, it is capable of inducing a similar metamorphosis in another compound, if placed in contact with it.

The true explanation of this fact appears to be, that the particles or molecules of the exciting body or ferment, being in a condition of change, and therefore in motion, communicate to the molecules of the body placed in contact with them an amount of motion sufficient to destroy the balance of the existing affinities; which in organic compounds is easily done, the chemical equilibrium being very unstable; and thus gives rise to a new play of affinities and the production of new compounds, as when sugar by contact with yeast is resolved into alcohol and carbonic acid.

But in addition to metamorphoses of the kind just alluded to, which, in the various ferments at least, commence spontaneously, air (at all events, at the commencement), moisture, and a certain temperature being the usual conditions, organic substances undergo very well marked decompositions when exposed to the action of heat and of some powerful re-agents; and it seems advisable here to give also a general account of such decompositions, as they admit of being classified under certain heads or rules generally applicable.

We shall here, therefore, briefly describe the changes produced on organic compounds: 1, by oxidation; 2, by the action of acids; 3, by the action of bases; 4, by the action of heat in close vessels, or the destructive distillation; and 5, by the contact of ferments.

Oxidation: a. direct.—The direct oxidation of organic compounds takes two distinct forms. The first is the familiar one of combustion, in which the action of the atmospheric oxygen is aided by a high temperature. The results differ according to the supply of oxygen. If there be an excess of air, or of oxygen, from any source, the whole of the carbon and hydrogen is converted into carbonic acid and water, which, along with uncombined nitrogen, are the ultimate products of the action of oxygen on organic matters. But if the supply of air be deficient, the hydrogen is oxidised in preference to the carbon, which is deposited as smoke, soot, or lampblack.

The second form of direct oxidation is that which is commonly called decay, but which Liebig proposes to call Eremacausis (*i.e.*, slow combustion), and which takes place when organic matter is exposed to air and moisture. In dry air it does not occur.

One of the most familiar examples of this kind of oxidation is that decay of wood by which it is slowly converted into a dark brown powder—ulmine. In this process, as De Saussure has shown, the wood absorbs oxygen, and produces an equal volume of carbonic acid along with water, and the residue—ulmine. As, in combustion, the oxygen combines by preference with hydrogen, so also in eremacausis there is every reason to believe that the absorbed oxygen combines with the hydrogen of the wood, and that an equivalent quantity of oxygen, also derived from the wood, is given off in the form of carbonic acid. Now, since wood may be represented as composed of carbon and the elements of water, and as water and carbonic acid are two of the products of eremacausis, it might be supposed that the water was ready formed in the wood, and that the absorbed oxygen had combined with the carbon. But it has been shown that, in presence of hydrogen, carbon does not at the ordinary temperature combine with oxygen, for which its affinity is less powerful; and besides, in the decay of wood, the proportion of carbon in the residue (the ulmine) is constantly greater than in the wood. Thus oak wood, $C_{36} H_{22} O_{22}$ yield in one stage of decay, ulmine, the composition of which agrees with the formula $C_{35} H_{20} O_{20}$; and in a more advanced stage, an ulmine of the formula $C_{34} H_{18} O_{18}$. Here we see that for every 2 eqs. of hydrogen oxydised by the air, 1 eq. of carbon and 2 eqs. of oxygen have been separated; so that the per-centage of carbon in the residue constantly increases. and the final result of eremacausis would be a residue of carbon; were it not that, as the proportion of carbon in the ulmine increases, its affinity for the other elements, strengthened by its mass, becomes too powerful to be overcome by the oxygen of the air without the aid of heat. It has been suggested, however, by Liebig, that the process of eremacausis may occur under such circumstances as to leave at last a residue of pure carbon. The conditions necessary for this are still unknown; but if we suppose one of these conditions to be a semi-fluid state of the matter undergoing decay, and if we imagine the process to go on at a very slow rate indeed, the carbon thus eliminated might assume the crystalline form, and thus the diamond might be produced. This is a mere suggestion ; but it has more probability in its favour than any other theory of the production of the diamond.

Other examples of eremacausis are, the acetification of alcohol. and the process of nitrification in which ammonia undergoes eremacausis. These, as well as other instances, will be considered in their proper place.

Eremacausis is greatly promoted by heat and by the presence of alkalies. It is, on the contrary, arrested or retarded by cold, dryness, acids, and many salts, such as corrosive sublimate, which has been used to prevent the decay of wood.

There is one circumstance connected with eremacausis, or decay, as above described, which is worthy of special attention. It is, that a substance, in a state of eremacausis, if placed in contact with another, which is capable of undergoing this change, speedily causes the latter to enter into the same condition of change. This effect of contact may be compared, in one sense, to that of a body in combustion, which sets fire to other bodies ; but in ordinary combustion the high temperature plays an important part, while in eremacausis the effect appears to be due to the communication of motion, from the particles of the decaying body to those of the other substance, which motion, as in the case of fermentation, overturns the existing balance of affinities, unstable as it is in organic compounds, and gives rise to the formation of new products.

The process of eremacausis, or slow oxidation in the atmosphere, is one of very great practical importance, inasmuch as, by this means, the elements of dead organic matter are made to assume those forms—namely, the forms of carbonic acid, water, and ammonia—in which they are capable of contributing to the nutrition of new or growing vegetables.

A peculiar species of eremacausis is observed in the case of the simultaneous action of oxygen and ammonia on certain colourless vegetable products, which, absorbing these gases greedily, are thus converted into nitrogenised compounds of very fine blue or purple colours. Of this we have examples in orcine, erythrine, and phloridzine ; and there is good reason to attribute the formation of indigo, from a juice devoid of blue colour, to an action of this kind, since both oxygen and ammonia appear to be necessary to its production. The transformation of alloxantine or of uramile into murexide also depends on the simultaneous action of ammonia and oxygen.

b. Indirect Oxidation. The indirect oxidation of organic compounds may be effected in a variety of ways, as, for example, by nitric acid, the action of which we shall presently describe along with that of other acids; by certain salts, as by permanganate of potash, which converts sugar, for example, into oxalic acid; or by the employment of a mixture of bichromate of potash and diluted sulphuric acid, by which means salicine may be made to yield the hyduret of salicyle (oil of spiræa); by the action of sulphuric acid, and of peroxide of manganese, as when alcohol is converted into aldehyde; or, finally, by the combined action of heat and hydrated alkalies, as when indigo, heated with potash, gives rise to anthranilic acid, hydrogen being given off; or acetates, heated with baryta, yield marsh gas and carbonates. The use of fusion with caustic potash as an oxidising agent is an important means of obtaining a less perfect oxidation than is the result of some of the other processes; and it has lately led to some very interesting discoveries in animal chemistry.

2. *Action of Acids on Organic Compounds.* This action is very various; the two acids most frequently employed are the nitric and sulphuric acids, and, as might be expected, the former acts more as an oxidising agent than the latter.

When sugar, for example, is heated with nitric acid, the latter loses oxygen, for nitrous acid is given off in enormous quantity; while the elements of the sugar, by the action of the oxygen are made to combine so as to produce compounds of less complex radicals than that of sugar probably is. Among the products are water, carbonic acid, oxalic acid, and saccharic acid, besides others not yet investigated; but the three first sufficiently show the tendency of oxidation to promote the formation of less complex radicals.

When nitric acid acts on organic matters, there is generally found one acid, if not more, among the products, and in this way a large number of acids have been discovered. Examples of this are, mucic acid from gum; indigotic and carbazotic acids from indigo; margaric acid from stearic acid; suberic and succinic acids from oily acids, besides many others. It frequently happens that compounds, whether acid or neutral, formed by the action of nitric acid on organic matter, contain hyponitrous acid as a constituent, apparently substituted for some element. This is the case with nitrobenzide from benzine, and with nitronaphthalase, and a whole series of compounds discovered by Laurent in his study of the action of nitric acid on naphthaline. The carbazotic or nitropicric acid also appears to contain a compound of nitrogen and oxygen. Some organic bases, as morphia and brucia, strike a deep red colour with nitric acid.

When sulphuric acid is made to act on organic compounds, it chars a considerable proportion of them by virtue of its attraction for oxygen and hydrogen in the form of water. But in many cases it produces very different effects. Thus, by boiling with sulphuric acid and water, starch and lignine are converted into grape sugar. In other cases, the sulphuric acid seems to lose so much oxygen as to produce hyposulphuric acid, which enters into combination with an organic compound, forming a new acid, as when sulphuric acid acts on naphthaline, and forms sulphonaphthalic acid; or on benzoic acid, forming hyposulphobenzoic acid; or on alcohol under certain circumstances, when an acid is produced containing the elements of hyposulphuric acid and of a carbon-hydrogen. In other cases, the sulphuric acid combines unchanged with the organic compound, as in sulphovinic acid, which is a bisulphate of oxide of ethyle; sulphomethylic acid, and others.

Many organic compounds, heated with excess of sulphuric acid, are entirely decomposed, yielding water which combines with the acid, and other products which are disengaged. Thus oxalic acid is resolved into water, carbonic acid, and carbonic oxide; formic acid into water and carbonic oxide; alcohol into water, olefiant gas, and other products.

Several organic compounds are dissolved by sulphuric acid with the production of a fine red or purple colour. Salicine strikes a red colour with the acid, and cedriret, one of the constituents of tar, dissolves in it with a deep blue colour, as does also naphthalase.

Phosphoric acid may be employed in some cases to remove water from organic compounds, as it does not char them. Like sulphuric acid, it forms with oxide of ethyle an acid salt, known as phosphovinic acid.

Hydrochloric acid and its congeners have no very extensive action on organic substances. With alcohol, hydrochloric acid gas yields chloride of ethyle; and a current of this gas, passed through an alcololic solution of a fatty acid, gives rise to the compound of the fatty acid with oxide of ethyle, which would otherwise be obtained with difficulty. With oil of turpentine, oil of lemons, and some other essential oils composed of carbon and hydrogen, hydrochloric acid gas combines, forming solids resembling camphor. Pyroxanthine, a substance contained in tar, dissolves in strong hydrochloric acid with a fine and deep purple colour.

3. *Action of Bases on Organic Compounds.* Hydrated bases unite, of course, with organic acids; and when heated with neutral substances, they generally give rise to the formation of acids, such as acetic and oxalic acids, or even carbonic acid,

oxygen being taken from the water of the base, and hydrogen being disengaged, or, (if the organic body contain nitrogen,) hydrogen and ammonia. This property of hydrated bases is employed as a means of converting all the nitrogen of organic compounds into ammonia, and in this form determining its quantity.

The presence of bases greatly promotes the absorption of atmospheric oxygen by organic substances. This is the reason why alkalies assist eremacausis. The same effect is very conspicuous in the change which the salts of gallic acid (and some other acids) undergo when exposed to the air. A solution of an alkaline gallate absorbs oxygen very rapidly, and becomes very dark in colour, being oxidised in a far shorter time than if the acid had been uncombined.

4. *Action of Heat on organic Compounds in close Vessels.* This action is known under the name of the *destructive distillation.* It must be considered as a combustion with a very limited supply of oxygen, that namely afforded by the substance itself. A very great variety of compounds is produced, many of them very interesting and useful. The destructive distillation may be considered as it affects substances containing nitrogen, and substances devoid of that element. Many products are common to both cases, but many also are confined to one case, especially to that of nitrogenised substances.

The destructive distillation of non-nitrogenised substances has been chiefly studied in the case of wood, which, when heated in close vessels, yields a great variety of products: some, binary compounds, such as paraffine, naphthaline, eupione, water, carbonic oxide, carbonic acid, marsh gas, and olefiant gas: others ternary, such as acetic acid, $C_4 H_3 O_3$; hydrated oxide of methyle or pyroxylic spirit, $(C_2 H_3) O, HO$; lignone, xylite, mesite, and other volatile etherial liquids, composed of the same elements as pyroxylic spirit, and very similar to it in properties; creosote; picamar; capnomore; cedriret; pittacal, and pyroxanthine, besides many others, not yet properly investigated.

When fatty or resinous bodies are subjected to the destructive distillation, there are obtained, besides other compounds, two solid carbo-hydrogens: chrysene, $C_3 H$, and pyrene, $C_{10} H_2$; which also occur among the products of the distillation of coal.

This latter distillation may serve as an example, the best known, of the action of heat on nitrogenised organic bodies; for coal contains a certain although small proportion of nitrogen. The products, besides creosote, paraffine, naphthaline, and probably several others of those obtained from wood, include much ammonia, hydrocyanic acid; some peculiar non-nitrogenised acids, as carbolic acid, $C_{12} H_5 O, HO$, (a remarkable compound, having an odour resembling that of creosote, and yielding, when subjected to various re-agents, an extensive series of new compounds [Runge, Laurent];) rosolic and brunolic acids; and three very remarkable nitrogenised bases, containing no oxygen, namely, kyanol (*aniline*, *crystalline*), $C_{12} H_7 N$, leukol, $C_{18} H_8 N$; picoline, $C_{12} H_7 N$, (Anderson), which is, therefore, isomeric with aniline, besides a fourth, not yet fully investigated, pyrrol; finally, paranaphthaline, or anthracene, $C_{30} H_{12}$, and coal tar naphtha, which is used as a solvent for caoutchouc.

The distillation of animal matter, such as hoofs, horns, or bones, yields analogous results, but is characterised by the very large amount of ammonia which is obtained, animal matter being richer in nitrogen than coal is. This ammonia appears as carbonate, which salt is thus manufactured, and hence was and occasionally still is, called salt of hartshorn.

Many organic acids, when heated in close vessels to a certain temperature, short of the destructive distillation, undergo a remarkable decomposition; carbonic acid is given off, and there remains a new acid, which is called a pyrogenous acid, or pyro-acid. Thus meconic acid, at a certain temperature, yields carbonic acid and komenic acid: while komenic acid, if heated in its turn, yields carbonic acid and pyromeconic acid. We have also pyromucic, pyrotartaric, or pyroracemic and pyrocitric acids; citric acid yielding three pyro-acids, aconitic, (equisetic), itaconic and citraconic acids, and malic acid also yielding two, maleic and paramaleic or fumaric acids.

From the above statements, it is obvious, that the action of heat on organic compounds gives rise to a very large number of important products, of which only the most remarkable have been named. All will be described in their proper places.

5. *Action of ferments on organic compounds.* Of this action the best known and most important example is the fermentation of sugar, by which it is resolved into alcohol and carbonic acid.

The circumstances under which this metamorphosis occurs are these: the sugar must be dissolved, the solution must have a certain temperature, and there must be present a ferment, such as yeast or some analogous body. In the juice of the grape a ferment, the fibrinous or caseous constituent of the juice, is naturally present; and Gay Lussac showed that the contact of atmospherical air was necessary to commence the fermentation, but that this contact with the atmosphere might be only for a very brief period, after which air was no longer necessary. It is obvious that the air acts by inducing a state of change in the ferment, for if any ferment, previously exposed to the air, be added to a pure solution of sugar, fermentation will take place without the mixture being exposed to the air after the ferment has been added.

Berzelius and others conceive that the ferment acts by contact in some way not very clearly defined, by catalysis, as it is called, as they conceive sulphuric acid to do in the formation of ether from alcohol. But Liebig has proved that in this latter case the acid first combines with ether (oxide of ethyle) forming sulphovinic acid (bisulphate of oxide of ethyle), and that this compound at a temperature rather higher than that at which it is formed, is decomposed into hydrated sulphuric acid and ether which distils over. The same chemist has pointed out many other instances of the effect of contact, even in inorganic chemistry : such as the action of oxide of silver on peroxide of hydrogen, where the former compound, by contact with the latter, not only decomposes it, causing oxygen to be rapidly given off, but is itself decomposed, losing all its oxygen ; the solution in nitric acid of an alloy of platinum and silver, while platinum alone is insoluble in that acid ; or the action of carbonate of silver on certain organic acids, which cause a disengagement of carbonic acid, this disengagement being attended with a partial reduction of the oxide of silver.

These, and many other, more familiar cases, particularly those where a compound is decomposed with detonation in consequence of a slight touch, or gentle friction, a moderate elevation of temperature, or the contact of another substance (*e.g.* chloride of nitrogen with oil) all tend, according to Liebig, to establish the doctrine that in certain compounds the balance of affinities is unstable, and therefore easily overturned, either by chemical or by mechanical influences.

The compounds which are capable of fermentation or any similar metamorphosis, are all of them bodies in which such an unstable equilibrium exists : they are all, in point of fact, easily decomposed by many different agencies, such as heat, acids, bases, oxygen, chlorine, &c. &c. Now, we can offer no other explanation of these facts of fermentation than this, that when a body in a state of progressive change, the particles of which are consequently in a state of motion, is placed in contact with another body, the particles of which are in a state of unstable equilibrium, the amount of motion mechanically communicated to the particles of the latter from those of the former, is sufficient to overturn the existing equilibrium, and by the formation of a new compound establish a new equilibrium more stable under the given circumstances.

There is nothing unphilosophical in this explanation, and it is to be considered as the best theory of fermentation yet attempted. According to the view of Liebig, a ferment is merely a compound in a state of decomposition, capable of setting in motion, and thereby bringing also into a state of decomposition, the particles of another compound, the existence of which depends on a nice balance of affinities.

On the other hand the view adopted by Berzelius, according to which fermentation, and all the other phenomena of chemical change produced by contact are the results of a peculiar unknown force, the catalytic force, coming into action when certain bodies are placed in contact, appears unphilosophical, as, in the first place, assuming the existence of a new force where known forces would suffice to explain the facts ; and, secondly, as furnishing no real explanation, but merely acknowledging, indirectly, our inability to offer any such explanation. When we ascribe an effect to catalysis, we are only saying, in other words, that we cannot account for it ; catalysis is thus merely a convenient term for all that we do not understand. And to the use of the word in this sense, namely, as a name for the agent which produces certain effects, the agent itself being unknown, there would be no objection, were it not that catalysis has been employed to account for phenomena not only different from each other, but actually of an opposite kind. For example, platinum, in causing *the combination* of oxygen and hydrogen, is said to act catalytically, and the action of oxide of manganese, or oxide of silver in decomposing peroxide of hydrogen, that is, in causing *the separation* of oxygen and hydrogen, is also called catalytic. This example proves how loosely the word has been employed, and how vague are the views which have led to its introduction.

A variety of important and interesting processes come under the head of actions caused by ferments ; the production of alcohol from sugar, of oil of bitter almonds from amygdaline, and of lactic and butyric acids from cane of sugar or sugar of milk, are all examples of this ; and in each of these cases the ferment is peculiar. In the case of sugar it is yeast, or gluten undergoing eremacausis and putrefaction ; in the case of amygdaline it is emulsine, a peculiar modification of albumen ; and in the case of cane sugar or sugar of milk, when converted into lactic or butyric acid, it is caseine, the nitrogenised constituent of the milk.

The access of air is required at first to yield oxygen to the gluten, &c., which then entering into eremacausis, or if air be excluded, into putrefaction, are capable of acting as ferments.

In the actions induced by ferments, we are to distinguish those in which some external element or elements are added to those of the compound, which cases resemble ordinary decompositions, from those in which the elements of the decomposed body merely transpose themselves, producing new compounds. The latter are properly and strictly termed metamorphoses. Fermentations, in which oxygen is absorbed, are examples of eremacausis, and it has already been mentioned that a body in a state of eremacausis acts on other bodies as an excitant of the same change, that is, as a ferment

Indeed, most ferments, whether they induce eremacausis, or a more pure metamorphosis in other bodies, are themselves in a state of eremacausis, at all events in the commencement of the change.

The subject of fermentation and ferments will be hereafter more especially considered, in connexion with fermentescible compounds: here the subject is merely treated in a general way.

Putrefaction, under ordinary circumstances, partakes largely of eremacausis, and differs from the ordinary kind only in the offensive odour of some of the products, chiefly compounds of sulphur and phosphorus, as sulphuretted and phosphuretted hydrogen. When air is excluded, putrefaction goes on, provided moisture be present, and it is then a metamorphosis, giving rise, in the case of vegetable matter putrefying under water, or in the strata of mines, to gaseous products, such as marsh gas and olefiant gas, constituting with air the fire-damp, and carbonic acid, which is the choke-damp, of the miner.

Animal matter, in a state of putrefaction, as putrid flesh, blood, cheese, or wine, acts as a ferment, and is capable of causing the metamorphosis of sugar into alcohol and carbonic acid, as well as of inducing eremacausis, and also propagating a putrefactive decomposition analogous to its own. Thus, it is well known that fresh cheese, if inoculated with decaying cheese, soon passes into decay, spreading from the seat of the inoculation.

We shall, hereafter, see that it is probable that some poisons and miasmata act as ferments on the blood. The singular sausage poison of Wurtemburg is animal matter in a peculiar state of decay, and does not contain any poisonous *compound*, only a poisonous *state* or *condition;* and the same principle may hereafter be found to furnish the true explanation of contagions.

Fermentation, putrefaction, and eremacausis are all promoted by the same circumstances, and arrested by the same influences. Antiseptics are substances, which, by combining with the ferment, or a part of it, or even with the body to be fermented, prevent the continuance either of the decomposition in the ferment, or of the fermentation itself. Corrosive sublimate and arsenic, which are powerful antiseptics, combine with animal matter, and form with it stable compounds; creosote combines energetically with albumen, &c., &c.

In fermentation, properly so called, the elements of the ferment take no chemical share in the metamorphosis of the body acted on by the mechanical agency above explained. That body is resolved into two or more new compounds of less complex radicals. The elements of water may or may not take part in the change; when they do, as in the case of sugar, the weight of the products, in this case alcohol and carbonic acid, is equal to that of the sugar, *plus* a certain weight of water. As, when the water is passed in vapour over carbon at a white heat, the carbon is shared between the oxygen and hydrogen, producing carbonic acid (or oxide), and carburetted hydrogen, so in the metamorphosis of sugar, and other analogous cases, we have on the one hand an oxidised compound, (in the case of sugar represented by carbonic acid), and on the other a compound in which part of the carbon is united to all the hydrogen (in the case of sugar, the alcohol). Similar results are obtained when alcohol or acetic acid are metamorphosed by heat, and this may be viewed as a general character of the metamorphosis of non-nitrogenised bodies: namely, that the carbon is divided between the oxygen and hydrogen.

In putrefaction, again, the ferment plays a chemical part in the change, and two or more compounds, the ferment and the putrefying body or bodies, combine to give rise to new compounds, with or without the elements of water. Putrefaction is generally the characteristic transformation of nitrogenised compounds, and the very great tendency of such compounds to undergo transformations is well illustrated by the spontaneous metamorphosis of a solution of cyanogen in water. Such a solution contains the four principal elements of organic bodies; and its transformations may be said to be the only case of putrefaction which has been as yet carefully studied.

The solution after a time becomes brown and turbid, and deposits a dark matter, containing ammonia, united to a compound formed of the elements of cyanogen along with those of water. This matter being insoluble, undergoes no further change. Such a compound might arise from the reaction between 2 eq. cyanogen, and 4 eq. water : thus $2\,C_2N + 4\,HO = NH_3 + (C_4HNO_4)$; according to some, the brown matter contains no ammonia, and is $C_4N_2HO = 2\,C_2N + HO$.

Another change is that in which water is decomposed, each of its elements uniting with cyanogen, and producing cyanic and hydrocyanic acids ; thus: $2\,HO + 2\,C_2N = (C_2N, O + HO) + H, C_2N$.

Another metamorphosis gives rise to oxalic acid and ammonia. In this case, 1 eq. cyanogen acts on 3 eq. water; thus: $C_2N + 3\,HO = NH_3 + C_2O_3$.

But cyanic acid cannot exist in contact with water and other acids : it is instantly metamorphosed into bicarbonate of ammonia ; thus: $C_2NO + 3\,HO = NH_3 + 2\,CO_2$.

Towards the end of the process, when ammonia has become predominant, the cyanic acid produced undergoes a different metamorphosis. It now unites with water and ammonia, and may possibly for a time exist as hydrated cyanate of ammonia : but at all events that salt, if formed at all, is soon transformed into urea. $NH_3 + C_2NO + HO = C_2H_4N_2O_2$ = urea.

Again, the hydrocyanic acid gives rise to another brown solid body, containing cyanogen or paracyanogen (possibly mellone also), and hydrogen ; and, along with this, oxalic acid, urea, and carbonic acid, by metamorphoses already described.

Lastly, the hydrocyanic acid in contact with water, and an acid or an alkali (here oxalic acid or ammonia), undergoes another metamorphosis, and is transformed into formic acid and ammonia ; thus : $H, C_2N + 4\,HO = NH_3 + C_2HO_3, HO$.

Thus cyanogen, a binary compound, along with water, another binary compound, gives rise to no less than eight different compounds ; 1st, the black compound, containing the elements of cyanogen and those of water, possibly C_4HN_2O : 2nd, ammonia, NH_3 : 3rd, cyanic acid, HO, C_2NO. 4th, hydrocyanic acid, H, C_2N. 5th, oxalic acid, C_2O_3 : 6th, carbonic acid : 7th, a brown solid, containing cyanogen (paracyanogen) and hydrogen : 8th, formic acid, C_2HO_3, HO : and in addition to these, three bodies, formed by the combination of two of the above eight, and containing all the four elements ; namely, 9th, oxalate of ammonia : 10th, bicarbonate of ammonia : 11th, urea.

This striking example is well adapted to give a clear idea of the immense variety attainable, when, instead of two binary compounds, two ternary or two quarternary compounds, along with water, are concerned ; and of the slight modifications of external circumstances which are required to produce results so varied, all the above substances being produced in a liquid at the usual temperature.

It is hoped that the above sketch of the doctrine of the chemical changes and metamorphoses of organic compounds will suffice to enable the student to follow the individual processes and reactions, to be hereafter mentioned, which, owing to our limited space, we must treat with great brevity. We shall now conclude our introductory matter by some general observations on the doctrines now held by many chemists on the subject of the organic acids; after which we shall enter on the study of the known organic radicals.

ORGANIC ACIDS.

The acids met with in organic chemistry are principally compounds of carbon, hydrogen, and oxygen, although some do contain also nitrogen. They are distinguished from inorganic acids by their high atomic weight, and by the action of heat, which decomposes them all. As, in many of them, the oxygen they contain is a multiple by a whole number of the oxygen of the bases which neutralise them, so they are viewed as oxygen acids by those who consider true sulphuric acid to be an oxygen acid, $S O_3$, and oil of vitriol to be its hydrate, $H O, S O_3$. In the case of acetic acid, for example, the formula of which is $(C_4 H_3) O_3 H O$, the compound $(C_4 H_3) O_3$, unknown in a separate form, is called dry acetic acid, and the strong acetic acid is considered as its hydrate; and the analogy is supposed to be fortified by the fact that dry acetic acid, like dry sulphuric acid, contains 3 eq. oxygen, and neutralises 1 eq. of base, $M O$, containing 1 eq. of oxygen.

But a careful study of the organic acids leads us to apply to them the same theory which we have already adopted for the inorganic acids, and to consider them as compounds of hydrogen, with compound radicals, usually consisting of carbon, hydrogen, and oxygen. On this view, as oil of vitriol is $H, S O_4$, the strongest acetic acid is $H, (C_4 H_3) O_4$. It is true that this radical, $(C_4 H_3) O_4$, does not exist, or is not known in the separate form; but the same remark applies to dry acetic acid, $(C_4 H_3) O_3$, which on the old view is supposed to be combined with water, for it also is unknown in the separate state.

The existence of compound radicals in organic acids is not more difficult to imagine than that of $S O_4$ the compound radical of sulphuric acid, for $(C_4 H_3) O_4$, only differs from it in containing three elements instead of two; indeed, as some ternary organic radicals are known in the separate form, we actually derive an argument from organic acids in favour of the existence of compound radicals in inorganic acids. Thus, the radical or organic metal, kakodyle, forms kakodylic acid.

But we find, among organic acids, a much larger proportion which are bibasic, tribasic, in short polybasic, than occurs among inorganic acids. Referring to what was said of the monobasic, bibasic, and tribasic phosphoric acids, it will be easily understood that while acetic acid, for example, is monobasic, tartaric acid, malic acid, komenic acid, alloxanic acid, and others are bibasic; that citric acid and meconic acid are tribasic, and that saccharic acid is quinquebasic. And as the three modifications of phosphoric acid were described on the old view as monohydrated, bihydrated, and terhydrated, and on the new view, as containing, respectively, 1, 2, and 3 eqs. of hydrogen, replaceable by metals, so tartaric acid may be either $C_8 H_4 O_{10}, 2 H O$ or $C_8 H_4 O_{12}, H_2$; malic acid may be $C_8 H_4 O_8, 2 H O$ or $C_8 H_4 O_{10}, H_2$; and so on; while citric acid may be either $C_{12} H_5 O_{11}, 3 H O$ or $C_{12} H_5 O_{14}, H_3$, and meconic acid, $C_{14} H O_{11}, 3 H O$, or $C_{14} H O_{14}, H_3$; and lastly, saccharic acid may be $C_{12} H_5 O_{11}, 5 H O$; or $C_{12} H_5 O_{16} H_5$.

In such polybasic acids, there is always some hydrogen in the radical, of which it is a constituent, and some combined with the radical, and replaceable by its equivalent of metals. It is only this latter hydrogen, the amount of which affects the neutralising power of the acid.

Now, among the phenomena of the action of bases on organic acids, we have some facts which seem almost to demonstrate the existence of this replaceable hydrogen, as such, and thus to establish the new theory of acids. Thus, meconic acid, which is tribasic, forms, like tribasic phosphoric acid, three series of salts, in which 1, 2, or 3 eqs. of hydrogen are replaced by metal. But while the meconic acid, as well as the tribasic phosphoric acid, readily forms with oxide of the silver, the salt in which all the hydrogen is replaced by silver; it cannot form, or forms with difficulty, a similar salt with potash, with which it forms very easily salts with 1 and 2 eqs. of metal, and 2 or 1 eqs. of hydrogen. Here we have the apparent contradiction of a weak base, oxide of silver, neutralising the acid easily and completely; while a strong base, potash, leaves it imperfectly neutralised. This cannot, I think, be accounted for on the old view, and many similar cases might be mentioned. On the new view, such apparent anomalies disappear: for since the neutralising depends on the replacement of hydrogen by a metal, it is evident that an oxide which is easily reduced, or deprived of its oxygen by hydrogen, like oxide of silver, will most easily neutralise acid, while a difficultly reducible oxide, such as potash, cannot be so far reduced as to yield 3 eqs. of metal, so as to form the neutral salt.

There are other kinds of organic acids which are what may be called coupled acids; that is to say they contain an acid coupled with another body, which does not neutralise the acid, but accompanies it in all its combinations. Thus, in hyposulphonapthalic acid, $C_{20}\ H_8\ S_2\ O_5,\ H\ O$, we have hyposulphuric acid, S_2O_5, coupled with napthaline, $C_{20}\ H_8$, and the coupled acid neutralises exactly as much base as the hyposulphuric acid alone would do. Again, formobenzoilic acid $C_{16}\ H_7\ O_5,\ H\ O$, may be viewed as a coupled acid, consisting of formic acid $C_2\ H\ O_3,\ H\ O$ and oil of bitter almonds (hyduret of benzoyle) $C_{14}\ H_6\ O_2$, which neutralises just as much base as the formic acid alone. Those coupled acids which contain hyposulphuric acid, as is often the case, are formed by the action of oil of vitriol, or of anhydrous sulphuric acid, on organic bodies, when 2 eqs. of acid, losing 1 eq. oxygen, form hyposulphuric acid; which commonly unites with the organic matter *minus* 1 eq. hydrogen, that hydrogen having combined with the oxygen derived from the sulphuric acid.

In the following pages we shall adopt the arrangement of Liebig, which has the advantage of uniting those substances which are naturally allied in composition. It proceeds, in the first place, on the principle of describing, under each known or admitted organic radical, all the compounds derived from or closely connected with it. After having gone through these, it takes up the consideration of the best known organic acids, including the oily acids; then the neutral oils, fat, and essential; the resins; the non-nitrogenous colouring matters, bitter and extractive principles, nitrogenised colouring matters and their congeners; the organic bases; starch; gum; woody fibre; destructive distillation of wood, of lignite, of coal: nitrogenised and sulphurised vegetable principles, albumen, &c., the modifications of these in the animal kingdom: bile: nervous matter: gastric juice: saliva: excrements: urine: blood: lymph, &c. And the whole is wound up with considerations on the nutrition of plants and animals.

This arrangement is not a scientific one, and in the present state of our knowledge such an arrangement is, I fear, unattainable. But it is very convenient, and, by judicious grouping, very much facilitates the learning and the retaining in the memory of the immense mass of facts which at present constitute organic chemistry.

We proceed, therefore, to consider those organic radicals which are admitted by the best authorities, although they are not always known in the separate state. The first compound radicals that attract our attention are certain binary ones, already mentioned as binary compounds, but not in their character of radicals, in the first Part of this work; these are amide or amidogen, cyanogen, and carbonic oxide.

I. Amide. $NH_2 = Ad = 16 \cdot 19$.

SYN. *Amidogen.*—It has already been mentioned that certain compounds exist, in which we can hardly doubt that this substance is present. Thus, potassium or sodium, heated in dry ammoniacal gas, disengages 1 eq. of hydrogen, forming the compound KNH_2 or $Na\,NH_2$. When these are put into water, potash or soda is formed, while ammonia is set free: $K, NH_2 + HO = KO + NH_3$. Again, when oxalate of ammonia, NH_3, HO, C_2O_3 is heated, there are formed, water which distils over, and the compound $NH_2\,C_2O_2$ which remains behind: thus, $NH_3, HO, C_2O_3 = 2HO + NH_2\,C_2O_2$. The latter compound is called oxamide, and is a sparingly soluble white powder, neutral or indifferent in itself, but yielding, when digested with an alkali, ammonia, which escapes, and oxalic acid, which combines with the alkali. Or if oxamide be heated with diluted sulphuric acid, it yields ammonia which combines with the acid, and oxalic acid which crystallises in cooling. In both cases water is decomposed: thus $NH_2\,C_2O_2 + 2HO = NH_3, HO + C_2O_3$.

Now oxamide is interesting, as being the type of a class of compounds, all of which, when heated with an alkali or an acid, yield ammonia and an acid, the ammonia and the anhydrous acid together containing just 1 or 2 eqs. of water more than the compound which, with the aid of water, has yielded them. If we consider oxamide as $NH_2 + C_2O_2$; that is, as composed of amide (or ammonia *minus* hydrogen NH_2), and the radical carbonic oxide (or oxalic acid *minus* oxygen C_2O_2), then all its congeners are likewise compounds of amide, on the one hand, and an anhydrous organic acid, *minus* oxygen, on the other. On this view benzamide is benzoate of ammonia, *minus* water, $(NH_3 + C_{14}H_5O_3, HO) - 2HO = NH_2 + C_{14}H_5O_2$; or it is amide *plus* benzoyle (the radical of benzoic acid, $C_{14}H_5O_2$). Therefore, when benzamide is acted on by potash, ammonia is given off, and benzoate of potash is left; and when it is heated with an acid, a salt of that acid with ammonia is obtained, while benzoic acid crystallises. There are a good many similar compounds which are called amides, and are viewed as compounds of amide.

It is obvious that the distinctive characters of amide, which is not known in the separate form, are its powerful affinity for hydrogen, and its equally strong tendency to combine with radicals which have a very great affinity for oxygen, such as those already mentioned, potassium, sodium, the radical $C_2\,O_2$, and the radical benzoyle. It is, probably, on account of its having so great an affinity for elements of the most opposite kind, that we cannot obtain it in the separate form.

With hydrogen amide forms two compounds, ammonia, $Ad\,H$, and ammonium, $Ad\,H_2$. The former may be called, in this view, hydramide. The latter (as has been already explained at p. 67) is considered to be a compound metal.

It is very remarkable, that when ammonia or hydramide combines with an acid, the resulting compound is not a salt, unless the acid contain hydrogen. Thus, hydramide, with dry sulphuric acid, $S\,O_3$, forms a compound which is not sulphate of ammonia, and is not a salt at all. But if, instead of $S\,O_3$, we employ oil of vitriol, $H\,O,\,S\,O_3$, or $H,\,S\,O_4$, sulphate of ammonia, a true salt, is obtained.

Here we may conclude that $Ad\,H$, in contact with $H,\,S\,O_4$, takes the hydrogen, forming ammonium, and that the resulting salt is composed of $Ad\,H_2 + S\,O_4$; that is, a metal combined with the sulphuric acid radical, just as sulphate of potash is $K,\,S\,O_4$. In all the true salts of ammonia, therefore, $Ad\,H_2 =$ Am (Ammonium) occupies the place of a metal, and may be replaced by a metal: and even if we consider sulphate of potash to be $K\,O,\,S\,O_3$, we have only to view the sulphate of ammonia as $N\,H_4\,O,\,S\,O_3 = Ad\,H_2\,O,\,S\,O_3 = Am\,O,\,S\,O_3$, that is, sulphate of oxide of ammonium.

It must be borne in mind, however, that although all the chemical relations of these compounds confirm the ammonium theory, yet neither ammonium nor its oxide are capable of existing uncombined; for ammonium, when separated, is resolved into ammonia and hydrogen; and oxide of ammonium, when separated, assumes the forms of ammonia and water.

Of the chief compounds of amide, ammonia or hydramide has been previously described. It remains for us to direct attention to this substance as constantly present in the atmosphere in minute quantity, from whence it descends in the rain, being an absolutely indispensable agent in vegetation. We have already seen that the putrefaction and eremacausis of nitrogenised compounds yields carbonate of ammonia as a product. Its presence in the air is therefore certain, *à priori*, even although we cannot detect it until it is condensed and accumulated in rain. It is, however, absorbed from the air by almost all minerals and soils, especially aluminous and ferruginous soils; hence a trace of ammonia is often found where it is not expected, and where it has been erroneously believed to have been formed by the direct union of hydrogen and nitrogen. This is the true explanation of the very remarkable and accurate experiments of Faraday, which have lately been confirmed by Will and Varrentrapp.

As an ingredient of manures, ammonia is most valuable. Its action on growing vegetables will be hereafter explained.

Ammonia forms a large number of compounds with the oxides of metals, the chlorides of metals, of sulphur, and of phosphorus, and finally with salts in general. These belong rather to inorganic chemistry, and the limited size of this work forbids us to describe them in detail.

But it is proper here briefly to notice the compounds formed by amide with metals, inasmuch as amide is here viewed as an organic radical, and some of these compounds are very important in reference to organic chemistry.

Amide then forms compounds with potassium, sodium, mercury, copper, silver, and platinum. The two former are of a greenish olive colour, and their action on water has been described above. The amide or amidide of mercury, $Hg\,Ad$, is not known in a separate state, but forms with bichloride of mercury the salt called white precipitate, $Hg\,Ad + Hg\,Cl_2$.

This salt is prepared by adding ammonia to a solution of bichloride of mercury. When boiled with potash, it yields another salt, $Hg\,Ad + Hg\,Cl_2 + Hg\,O_2$. The amidide of mercury also combines with the basic sulphate, and the basic nitrates of the same metal, forming, with the basic protonitrate, the soluble mercury of Hahnemann.

The amidide of copper, $Ad\,Cu$, is only known in combination with the hyposulphate and with the nitrate of ammonia.

The amidide of silver, $Ag\,Ad$, is known in combination with the nitrate, sulphate, seleniate and chromate of ammonia.

But it is the amidide of platinum which offers the greatest interest, as it gives rise to several very singular compounds, exhibiting the characters of very powerful bases. These remarkable substances have been studied by Gros, Reiset, and very recently by Peyrone, but are yet far from being understood. We shall endeavour briefly to state what is known of them.

When bichloride of platinum, $Pt\,Cl_2$, is heated for some time to nearly the melting point of tin, it loses half its chlorine, and is converted into protochloride, $Pt\,Cl$, which forms a powder of a dirty brownish green colour, insoluble in water. By continued digestion in ammonia, with the aid of heat, the protochloride is first changed into a green crystalline compound, which finally dissolves entirely, forming a yellowish solution, which on evaporation deposits yellowish white prismatic crystals. The green crystalline compound, discovered by Magnus, contains the elements of protochloride of platinum and those of ammonia, $Pt\,Cl\,N\,H_3$; the yellowish white crystals, discovered by Reiset, contain twice as much ammonia and the elements of water, $Pt\,Cl,\ 2\,N\,H_3 + aq$.

These two compounds are very remarkable; neither of them contains ammonia as such; both are insoluble in hydrochloric and dilute sulphuric acids. But the green compound of Magnus dissolves in nitric acid, with evolution of nitrous acid, and the solution on cooling deposits white crystalline scales, while the liquid contains no ammonia. These white scales, discovered by Gros, are the nitrate of a new base, $Pt\,Cl\,N_2H_6O$; which may be derived from 2 eq. of the insoluble compound of Magnus, $Pt_2Cl_2N_2H_6$, by the loss of 1 eq. of protochloride of platinum and the addition of 1 eq. of oxygen. This base acts exactly like the basic oxide of a metal, or like oxide of ammonium, $N\,H_4O$, combining with acids and forming neutral salts. It not only forms salts with nitric and sulphuric acids and the like, but with hydrochloric acid it yields a heavy crystalline powder, which is a chloride, bearing the same relation to the base as chloride of ammonium, $N\,H_4Cl$ (sal ammoniac) does to oxide of ammonium. This chloride, therefore, is $Pt\,Cl\,N_2H_6Cl$, and the radical of the oxide or base and of the chloride, will be $Pt\,Cl\,N_2H_6$, corresponding to ammonium, $N\,H_4$. Although Gros did not isolate either the radical or its oxide, yet from the characters and composition of its salts, there can be no doubt of its existence. If we represent this radical, $Pt\,Cl\,N_2H_6$ by R, then we have

$R\,O =$ oxide, the base of the salts, analogous to $K\,O$ or $N\,H_4$
$R\,O + S\,O_3 = R + S\,O_4 =$ sulphate, analogous to $K,\ S\,O_4$
$R\,O + N\,O_5 = R + N\,O_6 =$ nitrate, analogous to $K,\ N\,O_6$
$R\,Cl =$ chloride, analogous to $K\,Cl$ or $N\,H_4,\ Cl$

The soluble crystalline compound of Reiset, $Pt\,Cl\,N_2H_6 + aq$.

when heated to 212°, becomes anhydrous, and is then $Pt Cl N_2, H_6$, that is, it has the same composition as the radical of the base and salts of Gros. But it is not this radical; on the contrary, it is the chloride of a different radical, $Pt N_2 H_6$, and its true formula is $Pt N_2 H_6 + Cl$.

This new radical is also perfectly analogous to ammonium, as may be exhibited in a tabular form as follows.

	Chlorine Compound.	Sulphate.	Nitrate.	Double Chloride with Platinum.
Ammonium $NH_4 = Am$	$Am\ Cl$	$Am\ S\ O_4$	$Am\ N\ O_6$	$Am\ Cl + Pt\ Cl_2$
Radical of Reiset $\}$ $Pt N_2 H_6 = R'$	$R'\ Cl$	$R'\ S\ O_4$	$R'\ N\ O_6$	$R'\ Cl + Pt\ Cl_2$

In the case of ammonium, we cannot isolate the oxide $Am\ O = N H_4 O$, as it instantly resolves itself into ammonia and water, $N H_3 + H O$. But the oxide of Reiset's platinum radical, $R'O, = Pt N_2 H_6 O$, or rather its hydrate $Pt N_2 H_6 O + aq.$ is easily obtained from the sulphate by adding just so much baryta as will remove the sulphuric acid, and evaporating the filtered solution in vacuo, when the hydrated oxide crystallises in colourless needles. This compound is strikingly analogous to hydrate of potash: it is a powerful caustic, attracts carbonic acid from the air as strongly as potash, and exhibits all the chemical characters of one of the strongest alkalies. Few compounds are so remarkable as this base. We shall call it the base *a*.

This singular compound may be viewed as containing the elements of protoxide of platinum, ammonia and water, $Pt\ O, 2\ N H_3, H\ O$. When heated to 212°, it loses its water and half its ammonia, leaving a compound $Pt\ N\ H_3 O$ or $Pt\ O, N\ H_3$, which appears to be another new base, *b*, combining with acids and forming salts which detonate when heated. This last compound, when heated in the air, burns like tinder, and leaves metallic platinum. It is the oxide of a third radical, *b*, $= Pt\ N\ H_3$.

With hydrochloric acid the base *a* of Reiset yields water and the original chlorine compound, thus: $Pt\ N_2 H_6, O + H\ Cl = Pt\ N_2 H_6, Cl + H\ O$. When this chloride is heated to from 265° to 290°, it loses ammonia, and there is left a yellow powder, discovered by Peyrone, which dissolves easily in hot water, and has the composition of the green insoluble crystalline compound of Magnus, $Pt\ Cl\ N\ H_3$, of which it is an isomeric modification. Indeed, the compound of Magnus, (although insoluble in hot water,) if boiled with a saturated solution of sulphate or nitrate of ammonia, dissolves and is deposited on cooling in yellow crystals. The yellow ammoniated protochloride of platinum of Peyrone readily dissolves in ammonia, and the solution yields fine colourless prisms of the original chlorine compound of Reiset, but apparently not containing 1 eq. of water of crystallization, which is said to be present in the yellowish white crystals obtained by Reiset from the green compound of Magnus.

When the yellow compound of Peyrone is acted on by nitrate of silver, it yields chloride of silver, and two new compounds containing nitric acid and platinum, one of which forms yellow octahedrons.

If the sulphate of Reiset's base, $Pt\,N_2H_6 + S\,O_4$ be acted on by iodide of barium, $Ba\,I$, there is formed sulphate of baryta, $Ba\,S\,O_4$, and a protoiodide of Reiset's radical, *a*, $Pt\,N_2H_6, I$. This iodide is soluble and crystallisable, and when boiled with water, loses ammonia, while a new iodine compound is precipitated, $Pt\,N\,H_3, I$, corresponding to the chlorine compound of Peyrone and to that of Magnus, both of which are $Pt\,N\,H_3\,Cl$.

This new iodine compound seems to be the iodide of the third radical, *b*, $Pt\,N\,H_3$; for when acted on by nitrate or sulphate of silver, it yields iodide of silver, and a nitrate or sulphate of this new radical or of its oxide, $Pt\,N\,H_3, I + Ag, S\,O_4 = Pt\,N\,H_3, S\,O_4 + Ag\,I$; and $Pt\,N\,H_3, I + Ag, N\,O_6 = Pt\,N\,H_3, N\,O_6 + Ag\,I$. These new salts may of course be represented as $Pt\,N\,H_3, O + S\,O_3$, and $Pt\,N\,H_3, O + N\,O_5$. With ammonia, these salts yield the nitrate and sulphate of Reiset's base *a*; and with hydrochloric acid they yield the yellow compound of Peyrone. This would indicate that the latter compound is $Pt\,N\,H_3, Cl$, the chloride of the radical $Pt\,N\,H_3$, while the green salt of Magnus may be the ammoniated protochloride of platinum $Pt\,Cl + N\,H_3$, or probably $Pt\,Cl, N\,H_3 + aq.$

Here we have, at all events, three very remarkable compounds, which contain platinum and the elements of ammonia. There is, first, the radical *b* last described, $Pt\,N\,H_3$; secondly, the radical of Reiset's base, *a*, $Pt\,N_2H_6$; and thirdly, the radical of Gros's base, $Pt\,Cl\,N_2H_6$.

Now we have given the history of these compounds somewhat minutely, because their existence throws much light on the nature of a numerous and important class of bodies, namely, the vegetable bases or alkaloids.

It will be observed, then, that the three new radicals above described all contain nitrogen, indeed, all contain the elements of ammonia, and are in their chemical relations entirely analogous to ammonium. Thus we have

	Radical.	Oxide.	Chloride.	Sulphate.
Ammonium.	NH_4	$NH_4 + O$	$NH_4 + Cl$	$NH_4 + SO_4$
Radical of Reiset's base *b*	$Pt\,NH_3$	$Pt\,NH_3 + O$	$Pt\,NH_3 + Cl$	$Pt\,NH_3 + SO_4$
Radical of Reiset's base *a*	$Pt\,N_2H_6$	$Pt\,N_2H_6 + O$	$Pt\,N_2H_6 + Cl$	$Pt\,N_2H_6 + SO_4$
Radical of Gros's base	$PtCl\,N_2H_6$	$Pt\,Cl\,N_2H_6 + O$	$PtCl\,N_2H_6 + Cl$	$PtClN_2H_6 + SO_4$

That the above formulæ represent in some respects truly the relation of these new bases to one another, is rendered probable by the fact that, while the radical and base *b* of Reiset differ from his radical and base *a* by containing 1 eq. of ammonia less, and these last from those of Gros by containing 1 eq. of chlorine less, we can actually transform the salts of Reiset's base *b* into those of his base *a*, by the addition of ammonia ; and the nitrate of Reiset's base *a*, by the addition of chlorine, yields a salt having the properties of the nitrate of Gros's base.

Now we have seen that ammonium may be viewed as a compound of amide, as $NH_2 + H_2 = Ad\,H_2$. May we not therefore suppose the new radicals to be also compounds of amide? May not Reiset's radical *b* be ammonium, in which 1 eq. of hydrogen has been replaced by 1 eq. of platinum, $Ad\left\{\begin{matrix}H\\Pt\end{matrix}\right.$? Again, just as we have seen in acids, viewed as hydrogen compounds, analogous elements added to the radical without affecting the neutralizing power of the acid, which remains the same as long as the *replaceable* hydrogen continues unchanged, we can suppose amide to be a basic radical, forming with hydrogen the base ammonia, but capable of taking up into the radical analogous elements without affecting the basic character of the ammonia, because we have now the hydrogen compound of an analogous, but more complex, basic radical. On this view, Reiset's radical *b*, may be the hydrogen compound of a basic radical, more complex than amide; in fact, amidide of platinum. Its formula would then be $Ad\,Pt + H$, and, although on this view it should correspond to ammonia, rather than ammonium, we cannot speak positively, as this is the least known of the three.

The other two radicals may be readily viewed as hydrogen compounds of complex amidides, as ammonium is the hydrogen compound of amidide of hydrogen.

Amide, NH_2 = Ad, with hydrogen, forms ammonia Ad H, and ammonium Ad H + H. In like manner, in the radical *a* of Reiset's salts, we have a complex amide, composed of amide and amidide of platinum, Ad + Pt Ad = Pt Ad_2, which, with 1 eq. hydrogen, may be supposed to form a compound analogous to ammonia, Pt Ad_2, H, and with two eq. of hydrogen, actually does form the radical *a* of Reiset, Pt Ad_2 H + H, exactly analogous to ammonium. So the radical of Gros may be derived from the complex amide Pt Cl Ad + Ad = Pt Cl Ad_2, which may form Pt Cl Ad_2 + H and Pt Cl Ad_2 H + H, the latter being the actual composition of the radical of Gros, corresponding to ammonium.

It may also be mentioned, that just as we may view ammoniacal salts as containing ammonia and water rather than ammonium and oxygen, so, the base *b* of Reiset may be, NH_3 + Pt O, analogous to NH_3 + H O in the salts of ammonia. If sulphate of ammonia be NH_3, H O + SO_3, the sulphate of Reiset's base *b* will then be NH_3, Pt O + SO_3, the protoxide of platinum here playing the part of water, or in other words, platinum playing the part of hydrogen, a substitution far from unnatural or improbable. Again, if we consider the ammoniaco-sulphate of copper to be $2\left.\begin{matrix}NH_3\\ Cu\,O\end{matrix}\right\} + SO_3$, then the sulphate of Reiset's base *a* wil be $\left.\begin{matrix}2\,NH_3\\ Pt\,O\end{matrix}\right\} + SO_3$, where platinum replaces copper, also a not improbable substitution. Reiset is disposed to adopt this view

The chloride of Gros's radical, Pt Cl N_2H_6 + Cl, may be viewed as a compound of bichloride of platinum with ammonia, Pt Cl_2 + 2 NH_3, and there is even reason to think that compounds of that radical may be obtained from the solution of bichloride of platinum in ammonia.

From the above remarks it will appear that every probable view which can be taken of these very interesting bases connects them with amide, ammonia, or ammonium, and it is for this reason that they have been treated of in this section. Many pages might be filled with details concerning them: but we have here only indicated those points which will help to elucidate the constitution of the vegetable alkalies.

That important class of compounds not only contains nitrogen, as an essential element, but exhibits the same analogy with ammonia which we have seen to exist in the compound platinum bases. Moreover, like these bases, the alkaloids do not appear to contain ammonia *as such;* and the probability is very great that their constitution is analogous to that of the bases now described. Recent researches by Berzelius, not yet published, are said to have established that the organic bases contain ammonia, coupled with other compounds.

II. Carbonic Oxide (as a Radical) ; $C_2O_2 = 28{\cdot}106$.

Syn.: *Oxalyle.*—There is good reason to believe that the radical of oxalic acid is formed of 2 eq. of carbonic oxide. It has long been known that carbonic oxide, in the sun's light, combines with chlorine to form phosgene gas or chlorocarbonic acid, CO, Cl or C_2O_2, Cl_2. This compound may be viewed as the chloride of the radical C_2O_2, or as carbonic acid in which 1 eq. of oxygen is replaced by chlorine, $C\left\{\begin{matrix}O\\Cl\end{matrix}\right.$, corresponding to $C\left\{\begin{matrix}O\\O\end{matrix}\right.$ or CO_2. But the existence of this radical is more securely inferred from the combinations it forms with oxygen, potassium, and amide.

CARBONIC OXIDE AND OXYGEN.

1. Oxalic Acid $(C_2O_2)O + HO$, or $C_2O_4, H = 44{\cdot}132$.

This acid occurs in nature, generally in the form of an acid oxalate of potash in certain vegetable juices, such as that of oxalis acetosella, also as oxalate of lime in many lichens. It is formed artificially by the action of nitric acid on sugar, starch, and many other organic compounds; also by the action of hypermanganate of potash on sugar, &c.

To prepare it, one part of pure starch is gently heated with 8 parts of nitric acid, Sp. G. 1·20 or 1·25. A very energetic reaction ensues, and much nitrous acid is disengaged; when this slackens, heat is applied, and continued till no more red vapours appear, when the liquid, if sufficiently evaporated, deposits, on cooling, a large quantity of crystals of hydrated oxalic acid. These are dried on a porous tile, to remove the mother liquor which contains much free nitric acid, saccharic acid, and other products. The dried crystals being dissolved in a little hot water, the solution, on cooling, deposits pure oxalic acid in four-sided prisms, which are colourless, very acid, very soluble in hot water, moderately so in cold water. These crystals contain 3 eq. of water of crystallisation, $C_2O_3, HO + 3aq$. When sharply heated, a part sublimes as dry acid, C_2O_3, HO. Oxalic acid is destroyed by heat without blackening, which serves to distinguish it from most other organic acids.

It is very poisonous, and is the cause of many fatal accidents from its similarity to Epsom salts, from which, however, it is easily distinguished by its very sour taste. The best antidote is prepared chalk administered in water, which forms the insoluble and inert oxalate of lime. It is easily detected by forming with lime water, or a soluble salt of lime, if no free acid be present, the very insoluble oxalate of lime, which when dried and heated to low redness is converted, without blackening, into carbonate of lime.

When oxalic acid, or any of its salts, is heated with oil of vitriol in excess, a brisk effervescence takes place, and the gas given off is a mixture of equal volumes of carbonic acid and carbonic oxide. This character furnishes another good means of recognising oxalic acid. The reaction is very simple, for $C_2O_3, HO + HO, SO_3 = (SO_3 + 2HO) + CO + CO_2$. The sulphuric acid seizes the whole of the water, and the anhydrous oxalic acid, C_2O_3 cannot exist in the separate state.

When the oxalates of certain protoxides, as those of cobalt and nickel, are heated in close vessels, the metal is left: carbonic acid being given off; $CoO, C_2O_3 = CO + 2CO_2$. Other oxalates, as that of manganese, give off carbonic acid and carbonic oxide, leaving the protoxide of the metal, $MnO, C_2O_3 = MnO + CO + CO_2$.

Oxalic acid forms salts with bases, many of which are insoluble. The insolubility of the oxalate of lime renders oxalic acid useful as a test for lime, and as a means of separating it, and determining its quantity, in analysis. As a test, it is commonly used in the form of oxalate of ammonia. It can only detect lime in neutral or alkaline fluids, the oxalate of lime being soluble in free acids.

The formation of oxalic acid by the action of oxidising agents on organic matters, is a partial oxidation of their carbon; when that oxidation is complete, carbonic acid is the result. The action of nitric acid on starch or sugar is complicated, and not so well understood as to admit of being expressed in the form of an equation; but the oxidation of sugar by permanganate of potash is very simple, and is thus represented, $C_{12}H_{10}O_{10} + 6(KO, Mn_2O_7) = 6(KO, C_2O_3) + 10HO + 12MnO_2$; that is, 1 eq. of anhydrous sugar, with 6 eq. of the permanganate, produces 6 eq. of oxalate of potash, 10 eq. of water, and 12 eq. of peroxide of manganese.

The most important oxalates are those of potash, lime, and ammonia. There are three oxalates of potash; the neutral oxalate, $KO, C_2O_3 + aq.$; the binoxalate, $KO, C_2O_3 + HO$,

$C_2O_3 + 2$ aq ; and the quadroxalate, $KO, C_2O_3 + 3$ ($HO, C_2O_3 + 4$ aq. The double oxalate of potash and oxide of chronium, described by me some years since, forms crystals which are black by reflected, deep blue, by transmitted light. The solution is green and red at the same time by day-light, crimson red by candle-light. Sir D. Brewster has described, in the *Edin. Phil. Trans.*, the very remarkable optical properties of this salt. The oxalate of lime is $CaO, C_2O_3 + 2$ aq. The oxalate of silver AgO, C_2O_3, detonates when heated, yielding, like several other oxalates of the noble metals, carbonic acid, and the metal. The oxalate of ammonia, $NH_4O, C_2O_3 +$ aq. is much used as a test. It crystallises very readily. When heated, it gives rise to a very remarkable compound, namely, *oxamide,* which is the type of a class. We shall here consider it.

Oxamide, $C_2H_2NO_2 = C_2O + NH_2 = 44{\cdot}296$.

When oxalate of ammonia is heated in a retort, it gives rise to a variety of products, and among these, to a white crystalline powder, insoluble in cold water, which is oxamide. It may be formed far more abundantly by the action of ammonia in solution on oxalate of oxide of ethyle, or oxalic ether. (See oxalate of oxide of ethyle.)

The remarkable character of oxamide is, that while itself neutral, and certainly containing neither oxalic acid nor ammonia, it is easily converted into oxalic acid and ammonia by boiling it either with strong acids or strong alkalies. In this reaction, the elements of 1 eq. of water are shared between the constituents of oxamide, that is, between the radical C_2O_2 and the radical amide, NH_2; for oxamide is nothing more than oxalate of ammonia, NH_4O, C_2O_3, minus 2 eq. of water, or NH_2, C_2O_2. A very small portion of an acid, for example, is sufficient to produce this effect on a large quantity of oxamide; for if the acid we add be neutralised by the ammonia produced, a corresponding quantity of oxalic acid is set free, and acts as any other acid would do. A minute proportion of an acid, therefore, here, appears to exert its influence on an unlimited portion of oxamide, but this is only in appearance. The fact, however, that the presence of a little oxalic acid enables oxamide to decompose water and to produce ammonia and oxalic acid, is very important, and tends to throw light on many similar changes in the organic kingdom, where the agency is not so apparent.

But oxamide is not the only product of the action of heat on oxalate of ammonia; for, besides carbonic acid, carbonic oxide, hydrocyanic acid, water, ammonia, and oxamide, all of which are or may be formed, there is produced, when the heat is so regulated that a honey yellow residue remains in the retort, a new acid, called oxamic acid, which constitutes that residue. It is mixed with a little oxamide, which is, however, left undissolved by hot water, in which the oxamic acid dissolves.

Oxamic acid forms soluble and crystallisable salts with lime, baryta, ammonia, and oxide of silver. Acids precipitate it from the saturated solution of its compound with ammonia, as a white sparingly soluble powder, the composition of which is $C_4H_2NO_5+aq.$ Although an acid, this compound exhibits all the relations of a compound of amide or amidogen, being converted by the action of alkalies at a high temperature into oxalic acid and ammonia. It differs, however, from oxamide in yielding 2 eq. oxalic acid and 1 eq. ammonia; for 1 eq. of oxamic acid, *plus* 3 eq. of water, contains the elements of binoxalate of ammonia. $C_4O_5, NH_2 + 3HO = (HO, C_2O_3) + (NH_4O, C_2O_3)$. This also explains its production :—

for 2 eq. Oxalate of Ammonia $2(NH_4O, C_2O_3)$	$=C_4H_8N_2O_8$
when acted on by heat,	
Yield 1 eq. ammonia	$= H_3N$
3 eq. water	$= H_3 \quad O_3$
1 eq. anhydrous oxamic acid	$=C_4H_2N \, O_5$
Together . . .	$C_4H_8N_2O_8$

Oxamic acid is certainly a very remarkable compound, being an acid amidide, or at least admitting of being so regarded, C_4O_5, NH_2. There are a few other examples of acid amidides, and we shall soon come to one, namely, *euchronic acid*, which is highly analogous to oxamic acid: being formed by the action of heat on mellitate of ammonia, along with a neutral amidide, *paramide*, similar to oxamide; and as oxamic acid yields acid oxalate, so euchronic acid yields acid mellitate of ammonia when long boiled with water. Cyanic acid may also be considered as, in some sense, an acid amidide; for $C_2NO, HO = C_2O_2, NH$; and $C_2O_2, NH + 2HO = NH_3, 2CO_2$; or, as is well known, cyanic acid, in contact with water, produces bicarbonate of ammonia.

Oxamic acid may further be viewed as a coupled oxalic acid, the adjunct in which is oxamide: for $C_4O_5NH_2$ is equal to $C_2O_3 + C_2O_2, NH_2$. Berzelius adopts this view, and is, generally speaking, favourable to the idea of coupled acids.

An alcoholic solution of oxalic ether, when ammonia is cautiously added till a precipitate of oxamide just begins to appear, yields a very beautifully crystallisable compound, long known as oxamethan, which is nothing else than oxamate of oxide of ethyle (see salts of oxide of ethyle). Its composition is $C_8\ H_7\ N\ O_6 = (C_4\ H_5)\ O + C_4\ H_2\ N\ O_5$. A similar compound exists with oxide of methyle, and was formerly called oxamethylan.

2. Carbonic Acid. $C\ O_2 = 22$.

This acid has been already described, and it is introduced here merely because it is formed by the complete oxidation of carbonic oxide; $C_2\ O_2 + O_2 = 2\ CO_2$.

CARBONIC ACID AND CHLORINE.

Chlorocarbonic Acid. $C\left\{\begin{matrix}O\\Cl\end{matrix}\right.$ or $C\,O + Cl = 49{\cdot}5$.

Syn. *Phosgene gas.* When equal volumes of chlorine and carbonic oxide are mixed and exposed to the sun's rays, they combine to form a colourless gas, of a pungent disagreeable smell, which acts strongly on the eyes. Sp. G. of the gas 3·399. When dissolved in water, it decomposes it, producing carbonic and hydrochloric acids. With alcohol and pyroxilic spirit it produces very remarkable compound ethers, to be afterwards described.

With ammonia, this acid forms sal ammoniac, and a white volatile crystalline substance, which is carbamide, $C\ O,\ N\ H_2$, produced as follows:—$C\ O,\ Cl + 2\ N\ H_3 = N\ H_4,\ Cl + C\ O,\ N\ H_2$.

Under the influence of the mineral acids, carbamide yields ammonia and carbonic acid, $C\ O,\ N\ H_2 + H\ O = C\ O_2 + N\ H_3$.

The chlorocarbonic acid may be considered as carbonic acid $C + \left\{\begin{matrix}O\\O\end{matrix}\right.$ in which half the oxygen has been replaced by its equivalent of chlorine, $C + \left\{\begin{matrix}O\\Cl.\end{matrix}\right.$

CARBONIC OXIDE WITH POTASSIUM.

Oxycarburet of Potassium: Rhodizonic Acid.

When potassium is heated in carbonic oxide gas, combination takes place, and a dark olive powder is formed, composed of carbonic oxide and potassium, in the proportions of $C_7 O_7 + K_3$, or $7\ C\ O + 3\ K$. This substance is formed in large quantity in the preparation of potassium from carbonate of potash and charcoal, and is the source of great loss as well as inconvenience. No such compound is formed with sodium, for which reason that metal may be more cheaply prepared than potassium.

The oxycarburet of potassium, if heated in the air, takes fire, but if exposed to moist air, or placed in water, it is converted into the potash salt of a new acid, rhodizonic acid, hydrogen being disengaged, $C_7\ O_7\ K_3 + 3\ H\ O = C_7\ O_7,\ 3\ K\ O + H_3$. As this hydrogen, however, is not pure, but contains carbon, the reaction is probably more complicated.

All the salts of rhodizonic acid are deep red, and when in crystals, reflect a green light. The rhodizonate of potash, when heated in solution in water, undergoes a very remarkable change, yielding free potash, oxalate of potash and croconate of potash, the latter being the salt of another new acid containing the same elements as rhodizonic acid in different proportions; this salt is $C_5\ O_4,\ K\ O$ or $C_5\ O_5,\ K$. The composition of rhodizonate of potash explains this re-action perfectly, for $C_7\ O_7 + 3\ K\ O = K\ O + K\ O,\ C_2\ O_3 + K\ O,\ C_5\ O_4$.

Croconic Acid. $C_5\ O_4,\ H\ O$? or $C_5\ O_5,\ H$.

This acid is named from the yellow colour of its salts. It is obtained from the croconate of potash, prepared as above, by the action of fluosilicic acid, which separates the potash. The acid is yellow, soluble in water and alcohol, and crystallises easily. All its salts are likewise yellow.

The rhodizonic acid, $C_7 O_7,\ 3\ H\ O$, may be viewed as a tribasic hydrogen acid, $C_7\ O_{10}\ H_3$: the croconic acid may also be viewed both as a hydrated oxygen acid, $C_5\ O_4,\ H\ O$, and as a hydrogen acid, $C_5\ O_5,\ H$. In this last form it connects itself with carbonic oxide, as it may be $5\ C\ O + H$. The same remark applies to another remarkable acid, containing the same elements, namely the mellitic acid.

Mellitic Acid. $C_4\ O_3,\ H\ O$ or $C_4\ O_4,\ H$.

This acid occurs, combined with alumina, in a very rare mineral, probably of organic origin, the mellite or honeystone. The acid is soluble, very sour, and permanent, not being altered by boiling nitric or sulphuric acids, nor by a heat of nearly 580°. The general formula of its salts, when dried at 212°, is $M\ O,\ C_4\ O_4\ H$, or $H\ O,\ C_4\ O_4\ M$. The salt of silver, however, at 212°, loses 1 eq. of water, and is left as $C_4\ O_3,\ Ag\ O$, or $C_4\ O_4,\ Ag$. According to the latter formula, the radical in this salt, heated to 212°, is a form of carbonic oxide, $C_4\ O_4 = 4\ C\ O$.

The crystallised acid C_4O_3, HO, or C_4O_4H, appears to unite with most bases without the separation of water, generally observed when salts are formed. And although the silver salt would seem to contain a different radical, yet it yields, when decomposed, the original mellitic acid.

The mellitate of silver may also be looked on as oxalate of silver AgO, C_2O_3, plus 2 eq. of carbon in the acid AgO, C_4O_3.

The mellitate of ammonia, NH_4O, C_4H_3, when heated in a retort, yields several new and remarkable products, When this salt, $NH_3, HO, C_4O_3 = C_4H_4NO_4$ is heated to 320°, it gives off ammonia and water, and there remains a mixture of two new compounds; a soluble one which contains *euchronic acid*, in combination with ammonia, and an insoluble one which is called *paramide*.

Paramide is a yellow solid, like clay. Its most remarkable character is that, when long boiled with water, it is converted into bimellitate of ammonia. This is the character of an amide, hence its name. The composition of paramide is C_8HNO_4, which readily explains, both its formation, and its conversion into bimellitate of ammonia.

If from bimellitate of ammonia, $NH_4O, C_4O_3 + HO, C_4O_3 = C_8H_5NO_8$
we subtract 4 eq. of water . . . . H_4O_4

there will remain . . . . . Paramide $= C_8HNO_4$

and of course, when reconverted into bimellitate of ammonia by long boiling, it merely takes up again these 4 eq. of water.

The soluble compound, euchronate of ammonia, when its solution is acted on by hydrochloric acid, deposits a white crystalline powder, which is euchronic acid, $C_{12}NO_6, 2HO$. Its formation is easily explained ; for

if from 3 eq. of mellitate of ammonia $= 3(C_4H_4NO_4) = C_{12}H_{12}N_3O_{12}$
we subtract 6 eq. water and 2 eq. ammonia $= H_{12}N_2O_6$

there will remain anhydrous euchronic acid $= C_{12}NO_6$

We can now see that the action of heat on 7 eq. of mellitate of ammonia gives rise to the following substances :—

2 eq. Paramide $= C_{16}H_2N_2O_8$
1 eq. Euchronic Acid $= C_{12}NO_6$
4 eq. Ammonia $= H_{12}N_4$
14 eq. Water $= H_{14}O_{14}$

7 eq. mellitate of ammonia $= C_{28}H_{28}N_7O_{28}$

When euchronic acid is boiled with water, it is dissolved and converted into an acid mellitate of ammonia.

1 eq. Euchronic Acid	=	$C_{12}\ N\ O_6$	
and 6 eq. Water	=	$H_6\ O_6$	
Together . .		$C_{12}H_6NO_{12}$	are equal to
3 eq. Mellitic Acid	=	$C_{12}H_3\ O_{12}$	
and 1 eq. Ammonia	=	H_3N	
Together . .		$C_{12}H_6NO_{12}$	

Euchronic acid is deoxidised by a plate of zinc, yielding a powder of a fine deep blue colour, which dissolves in ammonia or potash, with a splendid tint of purple. The blue powder is an inferior oxide of the same nitrogenised radical, which, combined with more oxygen, forms euchronic acid. The whole subject of mellitic acid and euchronic acid is most interesting, but mellitic acid is so rare that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin, and contains only 1 eq. of hydrogen less, and 1 eq. of oxygen more than succinic acid, we may hope to be enabled to obtain it artificially.

III. CYANOGEN. $C_2N = Cy = 26{\cdot}23$.

This very important compound has already been mentioned as a compound of carbon and nitrogen; but we have now to consider it in its far more important character of a compound radical. In fact, it was the first compound radical discovered, and the discovery of cyanogen by Gay-Lussac has proved more fertile in results than any other discovery yet made in Organic Chemistry. As cyanogen acts exactly like an element, we shall represent it by the symbol Cy, rather than by C_2N; using the latter only where the elements of cyanogen, and not itself, enter into changes and reactions.

Cyanogen is formed when animal matter is ignited along with carbonate of potash in close or covered iron vessels. The cyanogen being a gas, and combustible, would be dissipated, and in open vessels burned, were it not that it enters into combination with potassium derived from the carbonate, forming cyanide of potassium, K Cy, a salt not altered by a red-heat in close vessels. As this salt, however, is decomposed by the action of water, yielding carbonate of potash and of ammonia, hydrogen being set free, $(K, C_2N + 5HO = KO, CO_2 + NH_3, HO, CO_2 + H)$, it is necessary to convert the cyanide of potassium into a more stable compound. This is effected by the addition of iron, or of sulphuret of iron, the latter of which is formed by the mutual action of the sulphate of potash (always present in potashes), carbon, and the iron of the vessel. The iron, or its sulphuret, is readily dissolved by the aqueous solution of cyanide of potassium, yielding cyanide of iron, $\mathrm{Fe\,Cy}$, and sulphuret of potassium $\mathrm{K\,S}$, for $\mathrm{K\,Cy+Fe\,S=Fe\,Cy+K\,S}$. The elements of the cyanide of iron then form, with cyanide of potassium, the very permanent double cyanide, well known as prussiate of potash, properly ferrocyanide of potassium, which forms large and pure, transparent yellow crystals. From this compound, all the other compounds of cyanogen, and cyanogen itself, are prepared. Its empirical formula is $\mathrm{Fe\,Cy,\ 2\,K\,Cy+3\,H\,O}$, or $\mathrm{Fe\,K_2\,Cy_3+3\,H\,O}$. At 212° it loses all the water, and then contains only iron, potassium, and cyanogen $\mathrm{Fe+K_2+Cy_3}$. It may be conveniently viewed as a compound of cyanide of iron with cyanide of potassium; but we shall see hereafter that its rational formula is probably very different, and that it is a compound of potassium with a new radical, ferrocyanogen.

Cyanogen gas is best prepared by heating dried bicyanide of mercury, when the gas is given off, a part, however, assuming the solid form, and remaining behind as a black matter, paracyanogen, isomeric with cyanogen: or by heating a mixture of 6 parts dried ferrocyanide of potassium, and 9 parts bichloride of mercury, when chloride of potassium is formed by the action of the bichloride on the cyanide of potassium of the ferrocyanide, and the cyanide of mercury, if formed, is at once decomposed by the heat. $\mathrm{Fe\,Cy,\ 2\,K\,Cy+Hg\,Cl_2=Fe\,Cy,\ 2\,K\,Cl+Hg+Cy_2}$. The cyanide of iron is not altered. The gas may be collected over mercury, but is absorbed by water, with which it produces the various changes which have been minutely explained at pp. 277 and 278. It has a very pungent and peculiar smell, is colourless and transparent; and may be liquefied by a pressure of about 4 atmospheres. It is combustible and burns with a beautiful pink or purplish flame.

Cyanogen forms with hydrogen an acid, the hydrocyanic, $\mathrm{H\,Cy}$; with oxygen and the elements of water, three acids, $\mathrm{Cy\,O,\ H\,O}$; $\mathrm{Cy_2\,O_2,\ 2\,H\,O}$; and $\mathrm{Cy_3\,O_3,\ 3\,H\,O}$; of which the first is cyanic, the second fulminic, and the third is cyanuric acid. With chlorine, &c. it combines; with sulphur it forms a new radical $\mathrm{Cy\,S_2}$, sulphocyanogen; and with metals it forms salts, perfectly analogous with chlorides, such as $\mathrm{K\,Cy}$, $\mathrm{Fe\,Cy}$, $\mathrm{Ag\,Cy}$, $\mathrm{Hg\,Cy_2}$, &c. In short it plays exactly the part of a simple radical, and were it not easily decomposable, we should at once class it with chlorine as an element.

CYANOGEN AND HYDROGEN.

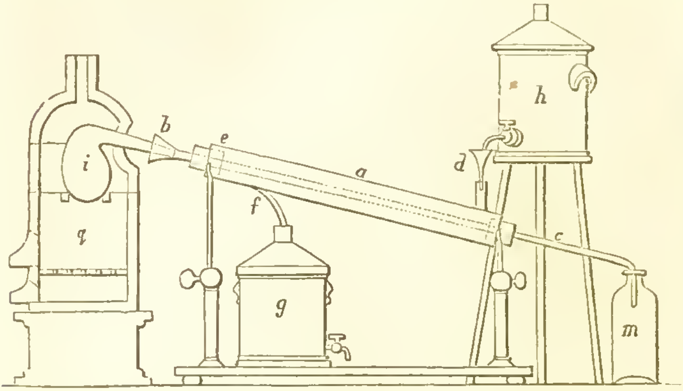
Hydrocyanic or Prussic Acid. $H\,Cy = 27{\cdot}23$.

This acid may be obtained by a great variety of processes; but the easiest, most economical, and most certain, is to act on the ferrocyanide of potassium with diluted sulphuric acid. The process requires to be slightly modified, according as our object is to prepare the dry or anhydrous acid, or the diluted aqueous solution of it used in medicine.

1. *Anhydrous Acid.*—To prepare this acid, 15 parts of powdered ferrocyanide are to be distilled at a gentle heat with a mixture of 9 parts of oil of vitriol, and 9 of water, and the product is to be received in a convenient receiver placed in a freezing mixture, and containing 5 parts of chloride of calcium in small lumps. As soon as liquid enough has distilled to cover the chloride, the distillation is stopped, and the hydrocyanic acid, deprived of water by the chloride of calcium, is to be decanted into a dry and well-stopped bottle. It may also be obtained by distilling, under similar circumstances, cyanide of potassium with dilute sulphuric acid. In both cases, the acid is formed by the reaction of sulphuric acid on cyanide of potassium, or its elements. $K\,Cy + H, SO_4 = K, SO_4 + HCy$. Dry hydrocyanic acid is a limpid and colourless liquid, of Sp. G. 0·6967 at 66°; at 59° it becomes a fibrous mass, in consequence of the presence of a trace of water; and at 80° it boils; the density of its vapour is 0·9476. It is inflammable, and has a very peculiar and disagreeable smell and taste. It is the most energetic poison known, one drop introduced into the mouth being sufficient to destroy an animal of considerable size. When pure it is soon spontaneously decomposed, depositing a dark brown solid; a trace of sulphuric acid causes it to keep perfectly. When in contact with the strong mineral acids and water, it is decomposed, being converted in ammonia and formic acid; $H, C_2N + 4\,HO = NH_3, HO + C_2\,HO_3$.

2. *Medicinal or diluted Hydrocyanic Acid.*—This may be prepared by simply diluting the anhydrous acid with the required proportion of water, adding, for example, 97 grains of water to 3 of the acid, to obtain an acid of 3 per cent.; which is about the average strength used in medicine. In round numbers, to one part, *by weight*, of dry acid, 32¼ parts of water, by weight, are to be added: or, to 1 *volume* of anhydrous acid, 22½ volumes of water. But as it is troublesome to prepare the anhydrous acid, it is best to distil 2 parts of ferrocyanide, with 1 of sulphuric acid and 2 of water, to dryness in a chloride of calcium bath, condensing in a Liebig's apparatus, (see woodcut)

in the receiver of which 2 more parts of water are placed. By this means we obtain 4$\frac{1}{2}$ parts of an acid, not anhydrous, but



far too strong for use, containing from 15 to 20 per cent. of dry acid. Its precise strength is ascertained, and it is reduced to the standard strength, in the following simple manner :

Any convenient quantity, say 50 or 100 grains, is weighed out, being added to a counterpoised vessel containing about 2 drachms of nitrate of silver, dissolved in 2 or 3 ounces of water. Let us suppose that we have dropped into this vessel 70 grains of our acid. This will be entirely converted into cyanide of silver, but we make sure by testing with a drop of nitrate of silver. The precipitate is then collected on a filter, well washed, dried at 212° on a weighed filter, and the increase in weight of the filter gives the weight of the cyanide of silver formed. Now this cyanide is formed as follows : $H\,Cy + (AgO, NO_5) = Ag\,Cy + (HO, NO_5)$. Therefore, 1 eq. of hydrocyanic acid, $H\,Cy = 27{\cdot}23$ produces 1 eq. cyanide of silver $Ag\,Cy = 134{\cdot}54$; or 1 grain of anhydrous hydrocyanic acid will yield almost exactly 5 grains of cyanide of silver ; for $27{\cdot}23 : 134{\cdot}54 :: 1 : 4{\cdot}94$. We may, therefore, safely assume that the weight of the cyanide of silver, divided by 5, gives the weight of anhydrous acid present with sufficient accuracy for all practical purposes. Now, we have used 70 grains of our dilute acid, the strength of which we wish to know. Let us suppose that our filter weighs, when empty, 20 grains, and with the cyanide of silver, dried at 212° till it ceases to lose weight, 100 grains. The difference, or 80 grains, is the weight of cyanide of silver obtained from 70 grains of our acid. Dividing this by 5, we have 16 grains as the weight of anhydrous acid contained in the 70 grains, and consequently combined with 54 of water.

Now, if we wish to state the per-centage of this acid, we obtain it by the calculation, 70 : 16 : : 100 : x, and $x = \frac{16 + 100}{70} = 22{\cdot}85$, so that our acid contains 22·85 per cent. of anhydrous acid. But if our only object be to reduce the acid to a standard strength, say that of 3 per cent., this last calculation is unnecessary, and we can proceed as follows: acid of 3 per cent. contains 3 grs. of dry acid and 97 of water; therefore, to find how much water is to be added to 16 grs. of anhydrous acid, 3 : 97 : : 16 : x, and $x = \frac{97 + 16}{3} = 517{\cdot}3$ grains of water, which must be added to 16 grs. of anhydrous acid, to bring it to the same strength. But our 70 grains of acid contain already, with the 16 of anhydrous acid, 54 grains of water, consequently we have only to add to these 70 grains 517·3 — 54 = 463·3 grains of water, and the same quantity of water for every 70 grains of the same acid. Of course, it is easy to calculate the water necessary for 1 or more ounces of the acid, when we have once found it for any given quantity. I have here supposed 70 grains, but with 50 or 100 the calculation is easier, and with a drachm by weight (60 grains), we have simple data for calculating how much water is required for any number of ounces or drachms, troy, of acid.

This beautiful and simple method of preparing the medicinal hydrocyanic acid, and ascertaining its precise strength, has been minutely described, because of its practical importance. It is so simple an operation, that any one may very soon learn to ascertain the strength of hydrocyanic acid, and it is very exact. Besides, no other method of obtaining a medicinal acid of uniform strength ought to be trusted to; and we ought never to attempt to obtain the acid of the standard strength by distillation, although many methods are given for this. I have never seen any one of these yield twice the same result; whereas by the above method we can prepare acid of exactly the same strength any number of times, and the acid prepared from the ferrocyanide, by sulphuric acid, keeps perfectly well. Of course, when we have added the calculated quantity of water to reduce the acid, it is proper to ascertain its strength once more, to make sure that we have made no error in our calculation. If it be acid of 3 per cent., it will yield 15 grains of cyanide of silver from 100 of acid.

There are two other methods which deserve to be mentioned, as, with pure materials and careful manipulation, they yield, in a few minutes, a standard acid. The first is that of Dr. Clarke, who adds to 1 eq. cyanide of potassium dissolved in water, 2 eq. Tartaric acid, which separates the potassium as cream of tartar, while diluted hydrocyanic acid remains dissolved. For every 100 grs. of water, 7⅓ grs. of cyanide of potassium and 16½ of crystallised Tartaric acid, are required. This is an excellent extemporaneous process, if we have pure cyanide of potassium, but that salt does not keep well, and even in its preparation it is apt to be decomposed, at least partially. It is, besides, an expensive salt. The other is the process of Everett, who suspends cyanide of silver in water, and adds an equivalent of hydrochloric acid. $Ag\,Cy + H\,Cl = Ag\,Cl + H\,Cy$. This is also a good extemporaneous process, 15 grs. of Ag Cy being used for every 100 of water, and 4 grs. of dry H Cl, that is, about 12 grs. of acid Sp. G. 1·21, being added. This process is also expensive, although the silver is not lost; but the chief objection is, that it is difficult to add the precise amount of hydrochloric acid which is necessary, and that an excess causes, *pro tanto*, a conversion of the hydrocyanic acid into formic acid and ammonia.

The medicinal acid has the smell and taste of the anhydrous, and is very poisonous, the average dose safe for an adult being 1 to 2 drops in a glass of water. It is much used as a sedative and anodyne, but, unless its strength and dose be perfectly known, it is a dangerous remedy. Fatal accidents have occurred from prescriptions, found, after experience, to act favourably, being made up in another place, or by the same druggist with a fresh stock; this fresh stock being exactly of the standard strength, while the previous acid had lost so much by keeping that the dose had been of necessity increased. There, danger actually arose from a too weak acid being used. Hence the necessity for the great exactness, for which rules are given above. In cases of poisoning by this acid, now unfortunately of very frequent occurrence, there is seldom time to administer an antidote; but when life is not extinct, we may confidently rely on the antidotes we possess. The best is the administration of two solutions, one of mixed sulphate of protoxide and peroxide of iron, and the other of carbonate of potash, as recommended by Messrs. Smith, Edinburgh,* by which the acid still in the stomach is rendered insoluble, being converted into Prussian blue. The symptoms already produced are best combated by ammonia inspired from a sponge, or taken, diluted, internally, and by other diffusable stimulants; also by the cold affusion.

Hydrocyanic acid is very easily recognised by its smell, and by its forming Prussian blue if acted on, in solution, successively, by proto-persulphate of iron, by potash, and by an excess of hydrochloric acid. The first two tests form the Prussian blue, the last, dissolving the excess of oxide of iron, brings the blue into view. Any liquid, suspected to contain hydrocyanic acid, ought first to be distilled with the addition of a little dilute sulphuric acid, and the tests applied to the first ounce that comes over. Nitrate of silver produces a white cloud of cyanide of silver, exactly like the chloride in appearance.

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* See *Lancet* for 1844, Vol. II. p. 41.

Hydrocyanic acid, with metallic oxides, gives rise to water and metallic cyanides. $H\,Cy + M\,O = H\,O + M\,Cy$: or $2\,H\,Cy + M\,O_2 = 2\,H\,O + M\,Cy_2$.

CYANOGEN AND OXYGEN.

1. Cyanic Acid. $Cy\,O, H\,O = Cy\,O_2, H = 43{\cdot}25$.

A monobasic acid; is formed when dry cyanide of potassium is heated in the air, when oxygen is absorbed, and cyanate of potash is produced. $K\,Cy + O_2 = K\,O, Cy\,O$ or $K, Cy\,O_2$.

When a stronger acid is added to this salt, the cyanic acid is set free, but immediately decomposes with water, producing ammonia which unites with the strong acid used, and carbonic acid which escapes as gas. $C_2\,N\,O, H\,O + 2\,H\,O = N\,H_3 + 2\,C\,O_2$. The carbonic acid carries with it a little cyanic acid, which forms dense white vapours, and has a pungent acid smell like that of strong acetic acid. Under all circumstances, free cyanic acid, in contact with water, is instantly destroyed.

It may, however, be obtained in the anhydrous state, according to the formula $Cy\,O_2 + H$, or as monohydrated acid, if viewed as $Cy\,O, H\,O$, by distilling cyanuric acid, $Cy_3\,O_6 + H_3$, or $Cy_3\,O_3 + 3\,H\,O$. This acid is isomeric with cyanic acid, and when heated, 1 eq. cyanuric acid splits up into 3 eq. cyanic acid, which appears in the receiver as a volatile, pungent, very corrosive acid liquid. This acid only keeps for a very short time, even in the freezing mixture in which it is condensed. If removed from the cold, it soon becomes turbid, then hot, boils violently, and with violent shocks, and is converted into a solid dense white body, like porcelain, quite insoluble and indifferent.

This is *Cyamelide*, another isomeric compound, containing the same elements in the same proportions, but differently arranged, possibly $C_2O_2 + N\,H$; for it yields, under the influence of water and strong acids, carbonic acid and ammonia, $(C_2\,O_2, N\,H + 2\,H\,O = 2\,C\,O_2 + N\,H_2)$ just as cyanic acid does. When distilled, it is reconverted into cyanic acid, another proof that it is isomeric with that acid.

CYANATES.

The salts of cyanic acid are all distinguished by the action on them of strong acids, which cause disengagement of carbonic acid, while ammonia may now be detected in the liquid. The cyanates of potash, ammonia, &c., are soluble, those of lead, silver, &c., insoluble.

Cyanate of potash is best formed by the oxidation of Liebig's cyanide of potassium,* which may easily be effected by adding litharge in proper quantity to the melted salt, $K\,Cy+2\,Pb\,O=K,\,Cy\,O_2+Pb_2$. The cooled mass is powdered and boiled with alcohol of 80 per cent., which on cooling deposits pure crystals of cyanate of potash, very similar to chlorate of potash. Or dried ferrocyanide of potassium, mixed with half its weight of peroxide of manganese, may be gently heated, spread out on an iron plate, when it burns like tinder, partly at the expense of the oxide of manganese, partly in the oxygen of the air. It is well stirred till every part has glowed, and the cold mass is treated with alcohol as above.

Cyanate of potash must be kept in sealed tubes, for in phials occasionally opened it is soon changed into bicarbonate of potash, ammonia being given off. $K,\,C_2N\,O_2+3\,HO=(KO,\,2\,CO_2)+N\,H_3$: Triturated with dried oxalic acid, this salt yields oxalate of potash and cyamelide. When acetic acid is added to a concentrated freshly made solution of cyanate of potash, the latter being in excess, there is deposited the acid cyanurate of potash,

$$Cy_3\,O_6\left\{\begin{matrix}K\\H_2\end{matrix}\right. \quad\text{or}\quad Cy_3\,O_3\left\{\begin{matrix}K\,O\\2\,H\,O\end{matrix}\right.$$

CYANATE OF AMMONIA.

a. *basic.* When dry ammonia and the vapour of cyanic acid are mixed, they form a light white solid, which is a cyanate of ammonia, containing more ammonia than is required for a neutral salt. This salt gives off ammonia when treated with alkalies, and cyanic acid when treated with sulphuric acid. But if dissolved in water, and the solution digested and evaporated, it yields crystals, which, although containing the elements of cyanic acid, ammonia, and water, exhibit neither of these characters of a cyanate, but are found to possess all the properties of *urea*, a product of the animal system.

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* The formation of this salt will be described below.

b. *anomalous cyanate of ammonia,* or urea, $C_2 N_2 H_4 O_2 = (C_2 N O, H O, N H_3)$. This remarkable compound exists in large proportion in healthy urine, and is extracted from it by evaporating it about 200° to a thin syrup, and adding about an equal volume of colourless nitric acid, Sp. G. 1·35, quite free from nitrous acid, which forms a very copious crystallisation of nitrate of urea, while the colouring matter is destroyed with brisk effervescence. If cold be applied, the colouring matter resists, and the nitrate is then very dark and very difficult to purify; cold ought, therefore, not to be used, and the nitrate of urea is deposited nearly white, having only a clear yellow tint. It is dissolved in water, after being recrystallised, and neutralised by potash or baryta. The whole is then gently evaporated to dryness, after separating as much nitrate of potash or of baryta as possible, and the dry mass digested in alcohol, which dissolves only the urea, and by spontaneous evaporation yields it in large transparent prismatic crystals. Should these not be colourless, the digestion of their aqueous solution with a little permanganate of potash, which has no action on urea, destroys the colouring matter entirely. Should an excess of that salt be added, a few drops of alcohol will instantly destroy it, and the filtered liquor will yield snow-white crystals of urea.

But although urea may thus be obtained (or by the action of oxalic acid on the urine, which forms a sparingly soluble oxalate of urea) in any quantity from urine, it is found much easier to prepare it artificially from cyanate of ammonia. Liebig recommends the following process, which I have found to succeed perfectly. 28 parts of dried ferrocyanide of potassium, and 14 of peroxide of manganese are mixed in powder and calcined, as above described, on a flat iron plate at a very low red heat, sufficient to keep up the glow which takes place. When this is over, the cold mass, powdered, is acted on by a moderate quantity of cold water, which dissolves the cyanate of potash. This is filtered off, and set aside. A fresh portion of cold water being added to the powder, to wash it, is also filtered, and in this liquid are now dissolved 20½ parts of sulphate of ammonia, and the solution is added to the first filtered solution of the cyanate. A large quantity of sulphate of potash is deposited, which is strained off, and the filtered liquid now containing, with some sulphate of potash, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea. The dry mass is digested in alcohol, which dissolves only the urea, and yields it from the first chemically pure and in any quantity, if the operation be carefully performed. Urea thus obtained is far cheaper than that extracted from urine.

The artificial production of urea from cyanate of ammonia, was discovered by Wöhler. It was, with the exception of oxalic acid, and of hydrocyanic acid, the first example of an organic product artificially formed, although many other cases are now known.

Urea forms 4-sided prisms, resembling nitre in appearance, and also in their taste, which is saline and cooling, exactly like that of nitre. It is soluble both in water and alcohol. When heated, it melts, gives off much ammonia, and finally solidifies, being in a great measure converted into ammonia and cyanuric acid.

Urea belongs to the class of organic bases, for it forms crystallisable compounds with several acids, such as nitric, oxalic, and acetic acids.

The nitrate, when impure, crystallises in scales of a high lustre; when pure, it forms opaque prisms, or a crystalline powder. It is sparingly soluble in cold water, but very soluble in hot water. Formula, $(C_2 N_2 H_4 O_2, HO, NO_5)$.

The oxalate forms long transparent prisms, very sparingly soluble. Formula, $(C_2 N_2 H_4 O_2, HO, C_2 O_3) = C_4 N_2 H_5 O_6$.

The acetate I have obtained as a mass of prismatic crystals, exceedingly soluble in water. Formula, probably $(C_2 N_2 H_4 O_2, HO, C_4 H_3 O_3) = C_6 N_2 H_8 O_6$.

Although urea combines with pure nitric acid, it is instantaneously decomposed by hyponitrous acid, yielding ammonia, water, and equal volumes of carbonic acid and nitrogen gases. $C_2 N_2 H_4 O_2 + NO_3 = NH_3 + HO + 2 CO_2 + N_2$. When acted on by strong acids, or alkalies, with the aid of heat, urea takes up the elements of water, and forms carbonate of ammonia, $C_2 N_2 H_4 O_2 + 2 HO = 2 (NH_3, CO_2)$. When urine is left in contact with the mucus usually suspended in it, the mucus entering into decomposition excites in the urea such a reaction with the elements of water, as very soon to convert the whole urea into carbonate of ammonia. Hence the reason why urine soon becomes alkaline, even if acid when voided. But if filtered from the mucus as soon as passed, it keeps unchanged, in clean vessels, for a long period.

2. Fulminic Acid. $Cy_2 O_2, 2HO = Cy_2 O_4, H_2 = 86{\cdot}5$.

A bibasic acid, unknown in the separate form. It is obtained in combination with oxide of mercury, or oxide of silver, by treating alcohol with the nitrates of these metals, and free nitric acid. A violent effervescence takes place, dense white vapours are disengaged, and a crystalline powder is deposited, which is fulminate of mercury or of silver. Both detonate powerfully by heat, friction, or percussion.

In the above reaction there are first formed, on the one hand, hyponitrous acid; on the other, aldehyde, and formic and oxalic acids. The fulminic acid is the result of a reaction between oxide of ethyle (ether) and hyponitrous acid, in presence of oxide of mercury or oxide of silver. $2\,NO_3 + (C_4 H_5)\,O = C_4 N_2 O_2 + 5\,HO = Cy_2 O_2, 2\,HO + 3\,HO$.

This acid cannot be isolated, being instantly decomposed when deprived of a fixed base. It forms two series of salts: neutral, with 2 eq. of fixed base, $Cy_2 O_2, 2\,MO$; and acid, with 1 eq. of fixed base and 1 of water $Cy_2 O_2, \left\{\begin{matrix} HO \\ MO. \end{matrix}\right.$ It also forms salts with 1 eq. of two different bases, of which one is always easily reducible, as oxide of silver, mercury, and copper, while the other may be difficult to reduce, such as baryta, potash, &c.

The fulminates of silver and mercury, $Cy_2 O_2, 2\,Ag O$, and $Cy_2 O_2, 2\,Hg O$, are examples of the first class. The acid fulminate of zinc $Cy_2 O_2 \left\{\begin{matrix} HO \\ Zn O, \end{matrix}\right.$ formerly supposed to be fulminic acid, is an example of the second; and the double fulminates of copper and silver, and of potash and silver, $Cy_2 O_2 \left\{\begin{matrix} Cu O \\ Ag O, \end{matrix}\right.$ and $Cy_2 O_2 \left\{\begin{matrix} KO \\ Ag O \end{matrix}\right.$ are examples of the third. No neutral fulminates exist with 2 eq. of a difficultly reducible oxide, such as potash, soda, baryta, &c.: nor do any acid fulminates occur with such bases. These very remarkable facts evidently point to some relation, not yet understood, between the oxygen of the base in a salt and the acid of that salt. Of course all the above formulæ may be written according to the theory of compound radicals and hydrogen acids.

To prepare the fulminate of mercury, which is much used for percussion caps, 1 part of mercury is dissolved in 12 parts of nitric acid, Sp. G. 1·36; 11 parts of alcohol at 80 per cent. are added, and the whole is warmed. A brisk reaction soon ensues, very thick white vapours are given off, and the salt is deposited in crystalline grains, mixed with a little metallic mercury. This salt explodes by friction, by percussion, or by heat, and it is a dangerous product, exploding occasionally without apparent cause. An explosion of this nature, not long since, destroyed the distinguished chemist, Mr. Hennell, who was preparing a large quantity in the open air. The fulminate of silver is prepared in the same way, only with 10 parts of nitric acid and 20 of alcohol. Caustic alkalies precipitate from its solution half the silver, forming double fulminates; and chlorides also only precipitate half the silver. Nitric acid, added to the solution, causes a deposit of acid fulminate of silver,

$$Cy_2O_2 \left\{\begin{array}{l} H\ \ O \\ Ag\ O \end{array}\right. \quad \text{or} \quad Cy_2O_4 \left\{\begin{array}{l} H \\ Ag \end{array}\right.$$

Hydrochloric acid added to fulminate of silver, gives rise to water, chloride of silver, hydrocyanic acid, and a new acid, chlorohydrocyanic acid C_2NCl_5, H_2. Thus—

$$C_4N_2O_2, 2AgO + 7HCl = 4HO + 2AgCl + C_2NH + C_2NCl_5, H_2.$$

3. Cyanuric Acid. $Cy_3O_3, 3HO = Cy_3O_6, H_3 = 126{\cdot}75$.

A tribasic acid discovered among the products of the distillation of uric acid. It is formed when solid chloride of cyanogen Cy_3Cl_3 acts on water: $Cy_3Cl_3 + 6HO = 3HCl + Cy_3O_6, H_3$. It is also formed when urea is heated so as to expel its ammonia. According to what has been stated of the composition of urea, it ought to yield cyanic acid when deprived of its ammonia; but at that temperature 3 eq. of cyanic acid, $3\,CyO, HO$, coalesce to form 1 eq. of cyanuric acid, $Cy_3O_3, 3HO$. When, again, acetic acid is added to cyanate of potash, in quantity insufficient to decompose the whole, there is deposited a salt which is an acid cyanurate of potash, $Cy_3O_3 \left\{\begin{array}{l} KO \\ 2HO. \end{array}\right.$

Finally, cyanuric acid is obtained by dissolving melame, ammeline, ammelide and melamine (see those substances) in sulphuric acid, and diluting and heating the solution, until it yields no precipitate with ammonia. On evaporation and cooling, the acid forms prismatic crystals, which are $Cy_3O_3, 3HO + 4aq$. When dissolved in hot nitric or hydrochloric acid, it is deposited, on cooling, in anhydrous octahedrons. When it has been prepared by heating urea, it is purified by dissolving it in oil of vitriol, and adding nitric acid, drop by drop, till the colour is entirely destroyed. An equal bulk of water is then added, and on cooling, pure cyanuric acid is obtained in crystals.

Cyanuric acid has a weak acid taste, and is sparingly soluble in cold water, more soluble in hot water. Unlike cyanic and fulminic acids, it is very permanent in the uncombined state. When heated in close vessels, it is entirely volatilised in the form of cyanic acid, of which 3 eq. are exactly equal to 1 eq. of cyanuric acid.

As cyanuric acid is formed when urea (cyanate of ammonia) is decomposed by heat, and when cyanate of potass is acted on by acetic acid, and as cyanuric acid, when heated, is resolved into cyanic acid, we have every reason to think that in the former cases, 3 eqs. of cyanic acid coalesce to form one of cyanuric acid; and that, in the latter case, 1 eq. of cyanuric acid is broken up into 3 eqs. of cyanic acid. $3\ (Cy\ O,\ H\ O) = Cy_3O_3,\ 3\ H\ O$.

Like other tribasic acids, cyanuric acid forms three series of salts, according to the formulæ:—

Hydrated Acid.	Salt with 1 eq. of fixed base.	Salt with 2 eq. of fixed base.	Salt with 3 eq. of fixed base.
$Cy_3O_3, 3\ HO$	$Cy_3O_3 \left\{ \begin{matrix} MO \\ 2\ HO \end{matrix} \right.$	$Cy_3O_3 \left\{ \begin{matrix} 2\ MO \\ HO \end{matrix} \right.$	$Cy_3O_3, 3\ MO$.

The salts with 1 and 2 eqs. of fixed base are acid; that with 3 eqs. is neutral. With potash and other similar oxides, only the two acid salts are known: with oxide of silver, the salts with 2 and 3 eqs. of oxide.

The three following salts, namely,

Cyanate of Silver,	Fulminate of Silver,	Cyanurate of Silver,
$Cy\ O.\ Ag\ O$;	$Cy_2\ O_2, 2\ Ag\ O$;	$Cy_3\ O_3, 3\ Ag\ O$

have exactly the same composition in 100 parts; and yet they are in properties entirely dissimilar; this can only be accounted for by some such difference in their formulæ, as is exhibited above. The acids of these salts are all mutually convertible: for when fulminate of silver is decomposed by a salt of ammonia, the fulminate of ammonia is transformed, like the cyanate, into urea; urea when heated yields cyanuric acid; and cyanuric acid when distilled is transformed into cyanic acid. All these circumstances favour the belief that all three are compounds of cyanogen, and that they differ in the absolute number of equivalents of their elements.

Cyamelide; $C_2\ O_2 + NH$?

But this is not the end of these transformations; for when cyanic acid is left to itself it becomes turbid and hot, and is soon converted with great heat, into an opaque white solid body, cyamelide, which has no acid properties; and which is also obtained as a white insoluble powder, when fused cyanate of potash is triturated with dried oxalic acid, in which case oxalate of potash is formed, and the cyanic acid, at the moment of being set free, is transformed into cyamelide. Cyamelide is neutral and insoluble in water and acids. It dissolves in aqua potassæ, ammonia being evolved, and the solution yields cyanurate of potash. Heated by itself it yields cyanic acid, which again passes into cyamelide; and when heated with strong sulphuric acid it forms sulphate of ammonia, while carbonic acid escapes: this action is identical with that which occurs when cyanic acid is acted on by water and by acids. All these observations prove that cyamelide is another isomeric modification of cyanic, fulminic, or cyanuric acid. Its probable formula is $C_2O_2 + NH$, and this, with 2 eqs. HO, yields bicarbonate of ammonia, just as cyanic acid, the formula of which is the same, does. The action of potash is probably this. $4\,(C_2O_2NH) + 3\,HO + 4\,KO = C_6N_3O_6, \left\{\begin{matrix}2\,KO \\ HO\end{matrix}\right. + 2\,KO, CO_2 + NH_3$; that is: 4 eqs. cyamelide, 3 eqs. water, and 4 eqs. potash, yield 1 eq. cyanurate of potash, 2 eqs. carbonate of potash, and 1 eq. ammonia.

The three oxygen acids of cyanogen may be fitly compared with the three phosphoric acids; and as we have hitherto made use of the older view of these acids, that which makes them hydrated oxygen acid, we shall, in this comparison, adopt the other theory, and speak of them as hydrogen acids.

	Monobasic.	Bibasic.	Tribasic.
Acids of Cyanogen . .	$Cy\,O_2 + H$	$Cy_2\,O_4 + H_2$	$Cy_3\,O_6 + H_3$
Acids of Phosphorus .	$P_2\,O_6 + H$	$P_2\,O_7 + H_2$	$P_2\,O_8 + H_3$

In the cyanic acids, both the radical and the replaceable hydrogen being doubled and trebled, the capacity of saturation increases in the same ratio. In the phosphoric acids, the capacity of saturation also increases with the replaceable hydrogen, but a great addition to the radical has no corresponding effect in increasing either the replaceable hydrogen or the neutralising power. Thus, if to tribasic phosphoric acid $P_2O_8 + H_3$ we add 2 eqs. of $P_2O_5 = P_4O_{10}$ we obtain $P_6O_{18} + H_3 = 3\,(P_2O_6 + H)$; that is, the acid becomes monobasic, but the quantity of base neutralised is the same after that addition as before. Notwithstanding this difference, however, the analogy between the monobasic, bibasic, and tribasic acids of cyanogen and phosphorus, as well as that between their salts, is most interesting and worthy of attention. As we believe that the phosphoric acids contain three different radicals, P_2O_6, P_2O_7, and P_2O_8, so we may admit that the three cyanic acids have each a distinct radical; only in this case the three radicals are alike in composition, and differ in their relative weight: the first being $C_2N = Cy$; the second C_4N_2

$= Cy_2$; and the third $C_6 N_3 = Cy_3$; or, in other words, these radicals are cyanogens, differing in molecular constitution, or three different allotropic forms of cyanogen. The relations of chlorine to cyanogen, and the existence of paracyanogen, countenance this idea.

CYANOGEN AND NITROGEN.

$$\text{Mellone} = Cy_3\, N = C_6\, N_4 = Me = 93.$$

Cyanogen, when it combines with nitrogen in the proportion of 3 eq. Cy to 1 eq. $N = C_6 N_4$, produces a very remarkable compound, discovered by Liebig, and called mellone, which being itself a well-marked compound radical, will be described as such, and not as a compound of cyanogen and nitrogen.

CYANOGEN AND CHLORINE.

Cyanogen forms two chlorides: one gaseous, but compressible, obtained by the action of chlorine gas on dry hydrocyanic acid; the other solid, formed by a spontaneous transformation of the former when kept in the liquid form in sealed tubes. Both are volatile and both contain cyanogen and chlorine, equivalent for equivalent. But the vapour of the solid chloride is three times denser than that of the other; and, moreover, the solid chloride, in contact with water, produces hydrochloric and cyanuric acids: while the gaseous chloride, under the same circumstances, gives rise to hydrochloric acid, and cyanic acid, the latter with water, at once passing into bicarbonate of ammonia, so that the final result is sal ammoniac and carbonic acid.

These considerations prove that the two chlorides are isomeric: that the first or gaseous chloride is $Cy\, Cl$; and that the solid chloride is $Cy_3\, Cl_3$, and is formed by the junction into one group of 3 eq. of the other; and we are consequently justified in extending this view to cyanic and cyanuric acids, and in supposing the vapour of the latter to be three times more condensed than the vapour of cyanic acid: and the cyanogen of cyanuric acid to be the cyanogen of the solid chloride, and three times denser than ordinary cyanogen.

CYANOGEN WITH BROMINE AND IODINE.

With these elements cyanogen readily combines when cyanide of mercury is distilled with bromine or iodine. The bromide and iodide are both volatile, and crystallisable, pungent and poisonous.

To judge by the density of their vapours, these compounds are $Cy\, Br$ and $Cy\, I$, corresponding to the liquid chloride, which is also very pungent and irritating to the eyes.

CYANOGEN AND SULPHUR.

Bisulphuret of Cyanogen. $Cy\,S_2 = 58{\cdot}5$.

When sulphocyanide of potassium, (see that salt) is acted on by chlorine or by dilute nitric acid, there is obtained an orange-yellow powder, which contains sulphur and cyanogen, and which is supposed by some to be bisulphuret of cyanogen, by others to contain hydrogen. This question will be considered hereafter, for whether this be so or not, there is a compound, possibly that compound, of sulphur and cyanogen, which acts as a radical, and is hence called sulphocyanogen. It will be described separately, since it is far more important as a radical than as a compound of cyanogen.

CYANOGEN AND METALS.

With metals, cyanogen forms compounds which in many cases are analogous to the chlorides of the same metal. When the metal is easily reducible, such as silver, mercury, or palladium, the cyanide is formed by the action of hydrocyanic acid on the oxide, or its salts: $M\,O + H\,Cy = H\,O + M\,Cy$. In the case of difficultly reducible metals, such as potassium, hydrocyanic acid seems to combine with the oxide, not being able to reduce it, until another cyanide is added, which tends to form a double cyanide.

Cyanide of Potassium, $= K\,Cy$ is best formed by heating to whiteness in close vessels the ferrocyanide of potassium, a salt which may be viewed as containing cyanide of iron and cyanide of potassium. The former is converted into insoluble carburet of iron; the latter remains unchanged, and may be mechanically picked out, or dissolved by hot alcohol of 60 p. c., which deposits it on cooling. Or, an alcoholic solution of pure and dry hydrocyanic acid is added to an alcoholic solution of potash; or, lastly, the vapours of hydrocyanic acid, formed on the process given at p. 299, are conducted into an alcoholic solution of potash, kept cool, when the salt is deposited.

It is white, and crystallisable in cubes. It has no smell when pure, but when exposed to moist air, smells of hydrocyanic acid. It is very poisonous. When heated it fuses easily, and is not altered by heat in close vessels. Heated in the air it absorbs oxygen, and is converted into cyanate of potash $K\,Cy + O_2 = K\,O, Cy\,O$. It is very soluble and deliquescent, and its solution, attracting carbonic acid from the air, gives off hydrocyanic acid: hence its smell.

Cyanide of Sodium is analogous to the preceding salt.

Cyanide of Zinc, Zn Cy, is obtained by adding hydrocyanic acid to acetate of zinc. It is a snow-white insoluble powder, which is used in medicine.

Cyanide of Iron.—Protocyanide of iron, Fe Cy, has not been isolated. There appears to exist a percyanide, also not yet isolated, $Fe_2 Cy_3$; and, according to Pelouze, there may be obtained an intermediate cyanide, $Fe_3 Cy_4$, analogous to the magnetic oxide of iron, as a green powder.

But although the cyanides of iron are little known, there are some very important compounds, especially those of two radicals, which contain those elements, namely, cyanogen and iron, along with hydrogen, and with metals. These will be described after we have gone over the simple cyanides of the metals.

Cyanide of Cobalt, Co Cy, is obtained as a brownish white precipitate, by adding hydrocyanic acid to the acetate of cobalt. Cobalt also forms compounds analogous to those of iron above alluded to, with cyanogen, &c.

Bicyanide of Mercury, $Hg Cy_2$, is easily obtained by dissolving red oxide of mercury in very dilute hydrocyanic acid, till the smell of the acid is destroyed. The liquid, rendered neutral, if necessary, by a few drops of hydrocyanic acid, yields fine crystals, on evaporation and cooling. Or it may be made by the action of three parts of persulphate of mercury on two of ferrocyanide of potassium dissolved in fifteen of hot water, which is boiled and filtered, and the filtered liquid on cooling deposits the bicyanide.

It forms regular prismatic crystals, permanent in the air, of a horrible metallic taste, soluble in water and alcohol. It is used for making cyanogen, also to prepare hydrocyanic acid by one process, and to yield the bromide and iodide of cyanogen.

Cyanide of Silver, Ag Cy.—Formed by the action of hydrocyanic acid or cyanide of potassium on nitrate of silver. It is exactly similar to the chloride, white, curdy, insoluble in water or acids, soluble in ammonia. It is decomposed by hydrochloric acid, yielding hydrocyanic acid.

Cyanide of Palladium, Pd Cy.—The affinity of cyanogen for palladium is most powerful, and hydrocyanic acid, or a soluble cyanide, when added to a salt of oxide of palladium, precipitate the cyanide as a grey powder. This property serves for separating palladium from other metals.

Cyanides of Gold.—The protocyanide, Au Cy, is formed by adding cyanide of potassium in excess to protochloride of gold, till a clear solution is formed, and then adding hydrochloric acid, which precipitates the protocyanide as a bright-yellow powder, very permanent, and soluble in cyanide of potassium.

The tercyanide, $An\,Cy_3$, is formed by the action of cyanide of potassium on terchloride of gold, and appears as whitish-yellow precipitate, soluble in cyanide of potassium, insoluble in acids.

DOUBLE CYANIDES OF THE METALS.

The insoluble metallic cyanides, such as those of iron, cobalt, copper, silver, gold, platinum, and others, dissolve readily in cyanide of potassium, or sodium, forming crystallisable double cyanides, which are not affected by soluble carbonates nor by chlorides, but are generally decomposed by acids, which precipitate the insoluble cyanide. If these double cyanides, which may be $2\,K\,Cy + m\,Cy$ ($m\,Cy$ being an insoluble metallic cyanide) are added to the solution of the oxide of another metal forming also an insoluble cyanide, this latter metal takes the place of the potassium, and a new double insoluble cyanide is the result. Thus $(2\,K\,Cy + m\,Cy) + 2\,M\,O = 2\,K\,O + (2\,M\,Cy + m\,Cy)$. (Here m may be iron and M copper or lead.) Now, as these double cyanides, thus precipitated, are of various and often characteristic colours, the ferrocyanide of potassium, $2\,K\,Cy + Fe\,Cy$, is extensively used as a test for metals.

The protocyanide of iron, the percyanide of iron, the percyanide of cobalt, and perhaps some others, not only form double salts with the elements of cyanide of potassium, but also produce very remarkable acids, by combining with the elements of hydrocyanic acid, that is, with hydrogen replacing the potassium of the double salt. Thus ferrocyanic acid is $2\,H\,Cy + Fe\,Cy$, and so on. In these compounds the hydrocyanic acid is no longer poisonous, and it is therefore highly probable that these acids, and their corresponding salts, really contain new and very peculiar radicals. The assumption of these radicals will alone enable us to classify or remember these compounds.

IV. FERROCYANOGEN. $Cy_3\,Fe = Cfy = 105{\cdot}87$.

We assume, then, the existence of this radical as the basis of ferrocyanide of potassium, or prussiate of potash. It is bibasic, combining with 2 eq. of hydrogen or of metals. The following formulæ expresses the composition of ferrocyanic acid, and of ferrocyanide of potassium, &c.

Ferrocyanic Acid $= Cfy,\,H_2 = Cy_3\,Fe,\,H_2 = 2\,H\,Cy + Fe\,Cy.$
Ferrocyanide of Potassium $= Cfy,\,K_2 = Cy_3\,Fe,\,K_2 = 2\,K\,Cy + Fe\,Cy.$
——— Iron $= 3Cfy,Fe_4 = 3Cy_3\,Fe,Fe_4 = 9\,Cy + 7\,Fe.$

It will be seen, by the two first compounds, that we may consider them either as compounds of the radical Cfy with hydrogen or metals, or as double cyanides. In the third, which is the formulæ of Prussian blue, we see that the iron exists in two different states, in one of which it cannot be detected by the usual tests. That form is the radical Cfy, which exists also in the two preceding compounds.

Ferrocyanic Acid. $Cfy, H_2=107·87$.

This very interesting compound is obtained by mixing a cold saturated solution of ferrocyanide of potassium with one quarter its volume of strong hydrochloric acid, and, agitating the mixture with half its bulk of pure ether, the ether rises to the surface, carrying with it, suspended, a white crystalline substance, which when washed with ether and dried, is ferrocyanic acid. It is soluble in water and alcohol, has a decidedly acid taste and reaction, and decomposes the alkaline carbonates, forming, with carbonate of potash, the ferrocyanide of potassium. The production of this compound by the action of hydrochloric acid on ferrocyanide of potassium is very easily explained. $Cfy, K_2 + 2\ H\ Cl = Cfy, H_2 + 2\ K\ Cl$.

Although this compound may be represented as a combination of cyanide of iron with hydrocyanic acid, $Fe\ Cy + 2\ H\ Cy$, there is every reason to believe that it contains no hydrocyanic acid. as such. For not only is it far more strongly acid, (and protocyanide of iron cannot be supposed to give acid properties to hydrocyanic acid,) but it is totally destitute of all poisonous properties, for both it and its salts may be taken internally without further effect than the laxative action common to most neutral salts.

Ferrocyanic acid, being bibasic, forms two kinds of salts: in the first the 2 eq. of hydrogen are replaced by 2 eq. of potassium, sodium, &c.; in the second, they are replaced by equivalents of two different metals: such as potassium and barium. An example of the first class is, $Cfy + K_2$; of the second $Cfy \left\{ \begin{matrix} K. \\ Ba \end{matrix} \right.$ Of all these compounds, by far the most important is the ferrocyanide of potassium, or prussiate of potash, from which all the compounds of cyanogen may be prepared, and which is manufactured on the large scale, being also used in the arts.

Ferrocyanide of Potassium. SYN. Prussiate of Potash. Anhydrous, $Cfy\ K_2$, 184·17. Crystallised, it is $Cfy, K_2 + 3\ H\ O = 211·2$.—This valuable salt is prepared by fusing animal matter, such as dried blood, hoofs, hair, horns, &c., or the animal charcoal remaining after such matters have been distilled, to obtain carbonate of ammonia, with potashes or pearlash, in iron vessels, as long as gas is disengaged. The melted mass is then withdrawn from the fire, and when cold, lixiviated with water, the solution digested with the insoluble part, filtered and evaporated, when it deposits, on cooling, yellow crystals; which by a second solution and crystallisation become quite pure.

The essential points of this process are, first, the presence of as much nitrogen as possible in the animal matter: hence fresh, dried, uncalcined animal matter is far preferable to animal charcoal: secondly, the presence of metallic iron or sulphuret of iron: the former is either directly derived from the vessels, which are rapidly corroded, or added as filings; the latter is formed from the iron of the vessels by the action of bisulphuret of potassium, which arises from the decomposition, by charcoal at a red heat, of the sulphate of potash contained in the potashes or pearlash; hence pure carbonate of potash is not adapted to this process. Thirdly, the exclusion of the air as far as possible, in order to prevent the oxidation and destruction of the cyanide of potassium formed.

The explanation of the process is very simple and beautiful, and we are indebted for it to the researches of Liebig. When animal matter is heated along with potash, cyanogen is formed, and combining with the potassium (set free at the same time by the action of carbon on potash) produces cyanide of potassium, a salt which is not decomposed by a red heat in closed vessels. At the same time, metallic iron and sulphuret of iron are present in the mixture, but not a trace of the ferrocyanide, previous to the action of water, for the very obvious reason, that the ferrocyanide is decomposed by a red heat, into cyanide of potassium and carburet of iron, nitrogen being disengaged.

If the cooled mass be now digested in water, the cyanide of potassium dissolves either the metallic iron with disengagement of hydrogen, or the sulphuret of iron, and the filtered liquid now contains the ferrocyanide.

Direct experiments have shown that cyanide of potassium dissolves either iron, oxide of iron, or sulphuret of iron, producing the ferrocyanide; $3\,K\,Cy + Fe + H\,O = (2\,K\,Cy + Fe\,Cy) + K\,O + H$. Or, $3\,K\,Cy + Fe\,S = (2\,K\,Cy + Fe\,Cy) + K\,S$. And it is has also been shown by Liebig that if the fused mass be lixiviated with alcohol, the residue, when treated with water, yields no ferrocyanide, while the alcohol contains none, but only cyanide of potassium.

Taking these facts into consideration, perhaps the best method would be to use pure carbonate of potash, free from sulphate, by which means no sulphuret of potassium would be formed, and the iron vessels would not suffer as they now do. The cyanide of potassium, being dissolved in water and filtered, should then be placed in contact with iron turnings in flat open vessels, when the third part of the potassium being oxidised by the air, the iron is rapidly dissolved, and a quantity of ferrocyanide obtained equal to that indicated by the cyanide of potassium present.

The ferrocyanide of potassium forms large honey-yellow, transparent, flat, quadrangular prisms, derived from a rhombic octahedron. It is very soluble in water, and forms precipitates in almost all metallic solutions, many of which are characteristic. Thus, with solutions of zinc and lead, it gives a white precipitate, with those of copper a chesnut brown, with those of peroxide of iron a deep blue, with protoxide of iron a pale blue, with those of barium and calcium whitish-yellow crystalline precipitates. The lead precipitate is Cfy, Pb_2; that of copper Cfy, Cu_2; those of barium and calcium $Cfy \left\{ \begin{matrix} K \\ Ba \end{matrix} \right.$ and $Cfy \left\{ \begin{matrix} K \\ Ca \end{matrix} \right.$; and that of zinc, $2\ Cfy + \left\{ \begin{matrix} Zn_3 \\ K \end{matrix} \right. + 6\ aq = Cfy, Zn_2 + Cfy \left\{ \begin{matrix} Zn \\ K \end{matrix} \right. + 6\ aq$. That of protoxide of iron is $2\ Cfy \left\{ \begin{matrix} Fe_3 \\ K \end{matrix} \right. = Cfy, Fe_2 + Cfy \left\{ \begin{matrix} Fe \\ K. \end{matrix} \right.$ All of these formulæ are easily referred to the general formula of the ferrocyanides, Cfy, M_2.

Ferrocyanide of Iron.—But the most remarkable of all these compounds is that formed with persalts of iron, namely Prussian blue. It is produced when ferrocyanide of potassium comes in contact with perchloride, or any salt of peroxide of iron. Now as ferrocyanogen is a bibasic radical, 1 eq. of it corresponds to 2 eq. of potassium, hydrogen, oxygen, chlorine, &c.; and as perchloride of iron, $Fe_2\ Cl_3$, contains 3 eq. of chlorine, 1½ eq. of ferrocyanide of potassium will be required to decompose 1 eq. of it, or, to avoid fractions, 3 eq. of ferrocyanide $Cfy_3\ K_6 = 3\ Cfy, K_2$, are required for 2 eq. perchloride of iron, $2\ Fe_3\ Cl_3 = Fe_4\ Cl_6$. The result is, $Cfy_3\ K_6 + Fe_4\ Cl_6 = 6\ K\ Cl + Cfy_3\ Fe_4$; and this last is the true formula of Prussian blue, although, from its tendency to combine both with ferrocyanide of potassium and with oxide of iron, its analysis offers great difficulties. The formula Cfy_3

Fe_4 or $Fe_4\ Cfy_3$ shows that Prussian blue corresponds to peroxide and perchloride (sesquioxide and sesquichloride) of iron, $Fe_2\ O_3$ and $Fe_2\ Cl_3$, for Cfy being bibasic is equivalent to Cl_2 or O_2, and consequently $Fe_4\ Cfy_3$ is equivalent to $Fe_4\ Cl_6$ or $Fe_4\ O_6$, that is, to $2\ Fe_2\ Cl_3$ and $2\ Fe_2\ O_3$. It must be admitted to be a very strong argument in favour of the existence of ferrocyanogen, as a bibasic radical, according to the theory of Liebig, that Prussian blue, in all other theories the most complex and anomalous compound in the whole range of chemistry, becomes quite normal and one of a series.

Ferrocyanide of potassium is employed to yield cyanogen and all its compounds. We have already seen how cyanogen, hydrocyanic acid, cyanide of potassium, cyanate of potash, urea, cyanic and cyanuric acids, and ferrocyanic acid are obtained from it. Cyanide of potassium, for testing, and to be used as a flux and in analysis, is best prepared, according to Liebig, by heating 8 parts of the dry ferrocyanide with 3 of pure carbonate of potash in an iron vessel till the fused mass is colourless. It is then poured off from the sponge of reduced iron, and kept in well-stoppered bottles. The reaction is as follows (representing the ferrocyanide, for convenience, as a double cyanide of iron and potassium): $2\ (Fe\ Cy,\ 2\ K\ Cy) + 2\ (K\ O,\ C\ O_2) = Fe_2 + 5\ K\ Cy + K\ O,\ Cy\ O + 2\ C\ O_2$. Hence the resulting salt contains 1 eq. cyanate of potash to 5 eq. cyanide of potassium. This very useful preparation, known as Liebig's cyanide of potassium, is not quite pure, containing cyanate of potash: but this does not interfere with its use.

Another very remarkable compound is produced by the action of a current of chlorine gas on the solution of ferrocyanide, if transmitted until the solution ceases to produce Prussian blue with perchloride of iron, yielding only a brownish-green colour, but no precipitate. The liquid now gives, on evaporation, beautiful deep hyacinth red crystals of a new salt, the ferridcyanide of potassium, discovered by Gmelin. This salt contains a new radical, ferridcyanogen.

V. Ferridcyanogen. $Cy_6\ Fe_2 = Cfdy = 211{\cdot}74$.

This radical has not yet been isolated. It is formed by the coalescence of 2 eq. of ferrocyanogen, and is tribasic. It forms an acid with hydrogen, and salts with metals.

Ferridcyanic Acid, $(Cy_6\ Fe_2) + H_3 = (2\ Cfy + H_3) = Cfdy,\ H_3 = 214{\cdot}74$.

This acid is obtained from the lead salt $Cfdy,\ Pb_3$, by the action of sulphuric acid. It is soluble in water, and by the action of sulphuretted hydrogen, is converted into ferrocyanic acid: $2\ Cfy, H_3 + H\ S = 2\ (Cfy, H_2) + S$. With bases it forms salts; as with potash the ferridcyanide of potassium.

Ferridcyanide of Potassium. SYN. Red prussiate of potash. —Its preparation has been described above. Its formula is $2\ Cfy + K_3 = Cfdy, K_3$; and it is quite anhydrous. Like the yellow prussiate, it forms precipitates with most metallic solutions, many of which are characteristic. With salts of peroxide or with perchloride of iron, it only strikes a brown or green colour, but with protochloride or salts of protoxide, it forms prussian blue. As the radical is tribasic, 1 eq. of it ought to be equivalent to 3 eq. of oxygen, chlorine, &c., and if we suppose the potassium in the ferridcyanide replaced by its equivalent of iron, we should have $Cfdy, Fe_3 = Fe_5\ Cy_6$; for $K_3\ Cfy_2 + 3\ Fe\ O = Fe_3\ Cfy_2 + 3\ K\ O$; and $Fe_3\ Cfy_2 = Fe_5\ Cy_6$. But, instead of this compound, there is formed prussian blue, the same we have above described as being formed by the action of yellow prussiate or peroxide of iron. In fact, when the red prussiate is added to a solution of a salt of protoxide, or to protochloride of iron, yellow prussiate is formed along with prussian blue and a salt of potash. Bearing in mind, as in all the above explanations, that 1 eq. ferridcyanogen Cfdy is equal to 2 eq. ferrocyanogen Cfy, and that, consequently, the red prussiate, $Cfdy, K_3$ may be equally well represented as $2\ Cfy, K_3$, then we have $2\ (2\ Cfy, K_3) + 4\ (Fe\ O, S\ O_3) = (3\ Cfy + Fe_4) + (Cfy, K_2) + 4\ (K\ O, S\ O_3)$.

The ferridcyanide of potassium may be viewed as ferrocyanide of potassium, *plus* a certain amount of ferrocyanogen; $2\ (Cfdy, K_3) = 3\ (Cfy, K_2) + Cfy$.

With salts of lead, ferridcyanide of potassium forms the ferridcyanide of lead, $Cfdy, Pb_3$.

VI. COBALTOCYANOGEN. $Cy_6\ Co_2 = Cky = 216{\cdot}52$.

Not yet isolated, but known in combination with hydrogen, potassium, &c. It is analogous to ferridcyanogen in constitution, and like it, is tribasic.

Cobaltocyanic acid $Cky\ H_3 = 219{\cdot}52$.—Obtained by the action of sulphuric acid on cobaltocyanide of lead Cky, Pb_3. It forms silky filaments, which are deliquescent and strongly acid.

Cobaltocyanide of Potassium, Cky, K —Is obtained by acting on a salt of oxide of cobalt with solution of cyanide of potassium and hydrocyanic acid, when hydrogen is given off and the new salt is obtained in crystals. The protocyanide of cobalt, precipitated on the first addition of cyanide of potassium, redissolves in an excess of that salt, forming a compound

$2\,\mathrm{Co\,Cy} + \mathrm{K\,Cy}$, or $2\,\mathrm{Co\,Cy} + 3\,\mathrm{K\,Cy}$. At all events there is enough of cyanide of potassium present to form the latter compound. The hydrocyanic acid, being now added, yields 1 eq. of cyanogen, converting the 2 eq. of protocyanide into 1 eq. of sesquicyanide of cobalt, while hydrogen is given off: $2\,\mathrm{Co\,Cy} + \mathrm{H\,Cy} = \mathrm{Co_2\,Cy_3} + \mathrm{H}$. Lastly, the sesquicyanide $\mathrm{Co_2\,Cy_3}$, with the 3 eq. of cyanide of potassium, $3\,\mathrm{K\,Cy}$, produces the cobaltocyanide of potassium, $\mathrm{Cy_6\,Co_2} + \mathrm{K_3} = \mathrm{Cky}, \mathrm{K_3}$. The crystals are isomorphous with those of the red prussiate of potash; they are yellow, soluble; their solution is not altered by acids, and gives, in solution of protoxide of cobalt, a beautiful rose-coloured precipitate, analogous probably to prussian blue; possibly, however, it may be $\mathrm{Cky}, \mathrm{Co_3}$. It precipitates many other metallic solutions, such as those of lead and silver.

Cobaltocyanide of potassium is a singularly permanent salt, resisting the action of the strongest acids; which is, in itself, a sufficient proof that it cannot contain cyanide of potassium as such. With the salts of nickel it forms a green precipitate, $\mathrm{Cky}, \mathrm{Ni_3}$, which is insoluble in boiling dilute acids. This property has been applied by Liebig to the separation of cobalt from nickel in analysis. All other metals being removed, an excess of potash is first added, and then hydrocyanic acid till the precipitate at first formed is dissolved, and the whole is then boiled. Hydrochloric acid is now added, and if no nickel be present, it produces no change, because it has no action on cobaltocyanide of potassium. But if nickel be present (of course by this time as cyanide) it is converted into chloride, and this is instantly precipitated by the cobaltocyanide of potassium as cobaltocyanide of nickel. Should there be more cobalt than nickel present, the whole nickel is precipitated, and the precipitate, acted on by potash, leaves the nickel as peroxide, while the cobalt is dissolved as cobaltocyanide, and may be determined along with the portion not precipitated for want of nickel. If, on the other hand, there be more nickel than cobalt, all the cobalt is contained in the green precipitate of cobaltocyanide of nickel, and may be dissolved by potash, and its quantity determined, while the nickel left by the potash as peroxide may be added to that left in the liquid for want of cobalt. Such is an outline of this very beautiful and refined method, which gives most accurate results.

VII. CHROMOCYANOGEN. $\mathrm{Cy_6\,Cr_2} = \mathrm{Cry}$.

This radical is little known. It is analogous to the two preceding, forming with hydrogen an acid, $\mathrm{Cry}, \mathrm{H_3}$, and with potassium a yellow crystallisable salt, Cry, K_3, which precipitates metallic solutions.

VIII. PLATINOCYANOGEN. $Cy_2Pt = Cpy = 151{\cdot}38$.

This radical is not known in the separate state. It forms with hydrogen a crystallisable acid of a gold or copper colour and metallic lustre, Cpy, H_2, which is very soluble and deliquescent. This acid is powerful, decomposes the carbonates, and produces platinocyanides. Platinocyanide of potassium, Cpy, K_2, is easily obtained by heating spongy platinum, or still better finely divided platinum black to low redness with twice its weight of dried ferrocyanide of potassium, and lixiviating with water; or by dissolving protochloride of platinum in hot solution of cyanide of potassium. It forms crystals yellow and metallic by transmitted, blue by reflected light. By the action of this salt on protonitrate of mercury, a cobalt-blue precipitate is formed, which, when heated in the fluid, becomes white, and is then pure platinocyanide of mercury, Cpy, Hg (?) This salt, acted on by sulphuretted hydrogen, yields the platinocyanic acid. A solution of platinocyanide of potassium acted on by chlorine, yields beautiful copper-like crystals of a new salt, which is either a double cyanide, $2\,K\,Cy + Pt_2\,Cy_3 + 5\,H\,O$; or the potassium salt of a new radical, $Pt_2\,Cy_5\,K_2 + 5\,H\,O$ (Knop.)

The platinocyanides of barium, strontium, and calcium, are easily obtained by the action of platinocyanic acid on these bases, and crystallise readily in beautiful greenish yellow colour, or in some cases green and red with metallic lustre.

IX. IRIDIOCYANOGEN. $Cy_3\,Ir = Ciy$.

This radical has not been isolated—it forms, with hydrogen, iridiocyanic acid Cy_3, Ir, H_2, which is obtained by the action of sulphuretted hydrogen on iridiocyanide of lead Cy_3 Ir, $Pb._3$

Iridiocyanide of Potassium, Cy_3 Ir, K_2, is obtained by the action of protochloride of irridium on cyanide of potassium. It forms colourless crystals; its solution gives, with salts of peroxide of iron, a deep indigo colour.

There appears to be a series of similar compounds formed by cyanide of palladium. The palladiocyanide of potassium corresponds to the platinocyanide, and its formula is Cy_2 Pd, K.

There is also reason to believe that manganese forms a manganocyanogen, corresponding to ferridcyanogen, $Cy_6\,Mn_2 =$ Cmy. The manganocyanide of potassium is probably $Cy_6\,Mn_2 + K_3 =$ Cmy, K_3.

From what has been stated in the preceding pages, it will be seen that cyanogen has a very great tendency to form cyanides containing 2 or 3 metals, and likewise cyanides containing one of these metals and hydrogen in the place of the other. As these latter compounds are very powerful acids, we are naturally led to consider them as hydrogen acids, in which the hydrogen is combined with radicals. This view has been adopted above, and we have seen reason to admit the following radicals :—

Platinocyanogen Cpy $= Cy_2\,Pt$
Palladiocyanogen Cpdy $= Cy_2\,Pd$
Ferrocyanogen Cfy $= Cy_3\,Fe$
Iridiocyanogen Ciy $= Cy_3\,Ir$
Ferridcyanogen = Cfdy $= Cy_6\,Fe_2$
Cobaltocyanogen = Cky $= Cy_6\,Co_2$
Chromocyanogen = Cry $= Cy_6\,Cr_2$
Manganocyanogen = Cmy $= Cy_6\,Mn_2$

It will be observed that there are three different formulæ among these radicals, namely, $Cy_2\,M$; $Cy_3\,M$; and $Cy_6\,M_2$; the first monobasic, the second bibasic, the third tribasic. No other view can at present be given of these compounds, of their acids, and of their salts, which is at once so satisfactory, so consistent, and so advantageous for the learner, as being adapted to assist the memory. It is true that the acids may be viewed as compounds of cyanide of a metal with cyanide of hydrogen (hydrocyanic acid), and their salts as compounds of two metallic cyanides. Thus, ferrocyanic acid, Cy_3Fe+H_2, may be said to be $2\,H\,Cy + Fe\,Cy$, and ferrocyanide of potassium, $2\,K\,Cy + Fe\,Cy$. Again, ferridcyanic acid may be $3\,H\,Cy + Fe_2\,Cy_3$ and its potassium salt $3\,K\,Cy + Fe_2\,Cy_3$: while platinocyanic acid and its potassium salt may be $H\,Cy + Pt\,Cy$ and $K\,Cy + Pt\,Cy$.

But the strong acid properties and inert nature of these acids, and the remarkable permanence, both of the acids and of the salts, are entirely inconsistent with the presence of so weak an acid and so frightful a poison as hydrocyanic acid, or of bodies so easily decomposed as hydrocyanic acid and cyanide of potassium. Besides, there are numerous double cyanides, such as $K\,Cy, Zn\,Cy$; $K\,Cy, Cd\,Cy$; $K\,Cy\,Cu_2\,Cy$, &c. &c. &c., which act as such ; being easily decomposed, and exhibiting no indications of containing radicals like those above described. We shall therefore not dwell on any other view, and merely allude here to the true double cyanides, as belonging more to the history of the metals, and less to that of the organic radicals.

PARACYANOGEN.

As an appendix to the metallic cyanides, we may here mention this compound, which is left behind as a dark-brown powder, when cyanide of mercury is heated in a retort. As cyanogen and mercury alone are given off, we should expect the salt to be dissipated by heat entirely; but this not being the case, it is evident that the residue, if it contain no mercury, must have the same composition as cyanogen, and be, in short, an isomeric modification of it—a solid cyanogen. Again, when cyanide of silver is heated, it gives off part of its cyanogen; it then glows, and, if soon removed from the fire, yields a peculiar residue, which is only partly dissolved by nitric acid. The insoluble residue appears to contain silver and cyanogen in the proportion $Ag\,Cy_3$, and it is probable that the cyanogen here is in the solid modification, of which 1 eq. is supposed to be formed by 3 eq. of cyanogen.

Whether, therefore, we admit paracyanogen as a separate radical or not, the two residues just mentioned contain carbon and nitrogen in the proportions to form cyanogen. It is also possible that some such compound may exist in cast iron and steel, which appear to contain nitrogen as well as carbon.

In treating of mellone, we shall see that doubts may be entertained of the existence of paracyanogen, and that the proportions of carbonic acid and nitrogen gases obtained in analysing the supposed paracyanogen may be derived from a mixture of mellone and carbon.

CYANOGEN AND SULPHUR.

X. SULPHOCYANOGEN. $Cy\,S_2 = Csy$.

SYN. *Bisulphuret of Cyanogen.*—When ferrocyanide of potassium is heated with sulphur, there is formed a new salt, the formula of which is $Cy\,S_2 + K$. This is sulphocyanide of potassium, which appears to contain the radical $Cy\,S_2$, or Csy. We cannot say that this radical is known in the free state, but by the action of chlorine on sulphocyanide of potassium there is formed a bright orange powder, which contains sulphocyanogen, mixed with some other bodies. Like the preceding radicals, sulphocyanogen, with hydrogen, forms a peculiar acid, the sulphocyanic or hydrosulphocyanic acid.

Hydrosulphocyanic Acid—$Cy\,S_2, H = Csy\,H$—is obtained by passing sulphuretted hydrogen gas through sulphocyanide of lead, Csy, Pb, suspended in water. The solution thus formed is highly acid, and has the odour of acetic acid. It strikes a blood-red colour with salts of peroxide of iron, and this property is found in all soluble sulphocyanides. The formula of this acid corresponds to that of cyanic acid, $Cy\,O_2, H$; and it may be viewed as cyanic acid, the oxygen of which has been replaced by sulphur. With metallic oxides, it forms the sulphocyanides of the metals; $Cy\,S_2, H + M\,O = Cy\,S_2, M + H\,O$.

Sulphocyanide of Potassium—$Cy\,S_2, K = Csy, K$.—The best process for obtaining this salt is to melt at a gentle heat (only raised at the end to low redness) 46 parts of dried ferrocyanide of potassium, 32 of sulphur, and 17 of pure carbonate of potash. The mass when cold is boiled with water, and the solution, being filtered and evaporated, deposits striated prismatic crystals of the salt, very similar in appearance, and in taste also, to nitre.

If not quite pure, it is purified by solution in alcohol and recrystallisation. In this process, the whole cyanogen of the ferrocyanide is first converted into cyanide of potassium, and then, by the taking up of sulpur, into sulphocyanide; while the iron is converted into sulphuret. As 1 eq. ferrocyanide contains 3 eq. of cyanogen and 2 of potassium, 1 eq. of carbonate of potash is added, and the 3 eq. of cyanide of potassium thus obtained take up 6 eq. of sulphur to form the new salt. $3\,K\,Cy + S_6 = 3\,(Cy\,S_2, K)$.

Sulphocyanide of potassium causes precipitates in some metallic solutions, but as many metallic sulphocyanides are soluble, the greater number of metals are not precipitated by this salt. With salts of peroxide of iron it strikes an intense blood-red colour, but causes no precipitate. With acetate of lead it gives yellow crystals, and with subacetate a white precipitate, and with salts of suboxide of copper also an insoluble white subsulphocyanide of copper. Sulphocyanide of silver is precipitated as a curdy white solid, when sulphocyanide of potassium is added to nitrate of silver. The other sulphocyanides are soluble.

When sulphocyanic acid is set free from its salts, by diluted acids, and exposed to heat, it is resolved, with the aid of the elements of water, into carbonic acid, bisulphuret of carbon, and ammonia. $C_2N\,S_2, H + H_2\,O_2 = \left.\begin{array}{l} C\,S_2 \\ C\,O_2 \end{array}\right\} + N\,H_3$. Compare this with the spontaneous decomposition of cyanic acid when set free from its salts: $C_2\,N\,O_2, H + H_2\,O_2 = \left.\begin{array}{l} C\,O_2 \\ C\,O_2 \end{array}\right\} + N\,H_3$. This shows that the view which considers sulphocyanic acid as cyanic acid, the oxygen of which has been replaced by sulphur, is confirmed by the similarity in the decomposition of these two acids; which, in this point of view, may be said to belong to the same type.

When sulphocyanide of potassium is mixed with 6 or 8 volumes of strong hydrochloric acid, hydrocyanic acid is given off, and a new crystalline acid is deposited, which, contains more sulphur, and may be called (hydro) persulphocyanic acid. $3\,(Cy\,S_2,\,H)$, that is 3 eq. of sulphocyanic acid lose $Cy\,H$, 1 eq. of hydrocyanic acid, and there remain 2 eq. of the compound $Cy\,S_3,\,H$, or persulphocyanic acid. The formula of its salts is $Cy\,S_3,\,M$. When the acid is dissolved in ammonia, it soon deposits sulphur, and the liquid retains a new compound $Cy_2S_5,\,H_2$ ($= 2\,Cy\,S_3,\,H - S$) combined with ammonia: on adding an acid, persulphocyanic is reproduced and deposited, while sulphocyanic acid remains in the solution:

$$Cy_2S_5,\,H_2 = \left\{ \begin{array}{l} Cy\,S_3,\,H \\ Cy\,S_2,\,H. \end{array} \right.$$

When solution of sulphocyanide of potassium is acted on by chlorine, or by nitric acid, a bright orange-yellow powder is deposited, which was long supposed to be sulphocyanogen; but it now appears to be a compound or mixture of sulphocyanogen, sulphocyanic acid, and water, in the proportions $3\,Cy\,S_2 + Cy\,S_2,\,H + H\,O = C_6\,N_3\,S_6 + (C_2\,N\,S_2,\,H) + H\,O = C_8\,N_4\,S_8\,H_2\,O$. This yellow compound undergoes a very remarkable change when heated: it gives off bisulphuret of carbon, sulphur, and a little persulphocyanic acid, and there is left in the retort a grayish-yellow powder, containing no sulphur, oxygen, nor hydrogen, and not decomposed by a low red heat. By a strong red heat it is dissipated, yielding a mixture of 3 vol. cyanogen to 1 vol. nitrogen.

This residue may be viewed as a cyanide of nitrogen $N\,Cy_3 = C_6\,N_4$, and as it plays the part of a radical, analogous to cyanogen, it is called mellone, and has the symbol Me. Its production from sulphocyanogen is easily explained: $4\,(C_2\,N\,S_2) = 2\,C\,S_2 + S_4 + C_6\,N_4$. If the orange-yellow compound which yields it be thrown into melted sulphocyanide of potassium the mellone actually seizes the potassium, expelling the sulphocyanogen, which is resolved into bisulphuret of carbon, sulphur, cyanogen, and nitrogen, all of which escape with effervescence. This is because mellone is not only a powerful radical, but also capable of resisting a strong heat.

XI. MELLONE. $Me = C_6\,N_4 = 92{\cdot}94$.

The preparation of this radical by the action of heat on impure sulphocyanogen, has been described above. It may also be obtained by heating to low redness the sulphocyanide of ammonium, as will be explained below. It appears as a grayish-yellow powder, which is capable of combining directly with potassium when heated with it, and of decomposing sulphocyanide of potassium, as before-mentioned. In both cases it forms a fusible, soluble, crystallisable salt, mellonide of potassium. When to the solution of this salt an acid is added, it causes a white gelatinous precipitate, which is an acid, sparingly soluble in water, the hydromellonic acid.

Hydromellonic Acid—$Me\,H = C_6\,N_4,\,H$—is best formed by mixing a hot solution of mellodine of potassium with strong hydrochloric acid, when, on cooling, hydromellonic acid is deposited as a snow-white powder. It is somewhat soluble in hot water, sparingly so in cold; it is a strong acid, and with acetate of potash, produces mellonide of potassium, displacing the acetic acid. If, however, a saturated hot solution of the mellonide be mixed with acetic acid, half the potash is removed, and on cooling, crystals of an acid salt are deposited, which, in the case of a hydrogen acid, is very unusual. It is possible, however, that hydromellonic acid may be bibasic, which would account for the fact of its forming an acid salt. This acid is very remarkable for its power of resisting heat, as it requires a full red heat to decompose and dissipate it.

Mellonide of Potassium—$Me,\,K = C_6\,N_4,\,K$—occurs as an accidental product in the making of sulphocyanide of potassium. It is best obtained by fusing at a low red heat, in a covered iron crucible, dried ferrocyanide of potassium, with about half its weight of sulphur, and adding, towards the end of the fusion, about 5 per cent. of dried carbonate of potash. The cooled mass is boiled with water, and the filtered solution concentrated, till, on cooling, it forms a semi-solid mass of minute needles, which are purified from sulphocyanide by washing with alcohol, in which the mellonide is insoluble. The mellonide may also be obtained by adding mellone to fused sulphocyanide of potassium, when, by the decomposition of the sulphocyanogen, an additional quantity of mellone is formed. In the first process, also, a portion of mellone is formed by the action of heat on the sulphocyanide of iron, produced at the commencement of the fusion; and this mellone acts, as in the second process, on the sulphocyanide of potassium, giving rise, in so doing, to an additional amount of mellone: hence, the advantage of adding some carbonate of potash, to prevent any loss of mellone. Finally, mellonide of potassium may also be prepared by adding 2 parts of dry subsulphocyanide of copper to 3 of fused sulphocyanide of potassium.

Mellonide of potassium is soluble in water, insoluble in alcohol. It has a bitter taste, and its crystals contain 5 eq. of water, of which 4 eqs. are expelled at 212°. When acted on by hydrochloric acid, it yields hydromellonic acid; when, by acetic acid, it gives the acid salt above-mentioned. By the action of mellonide of potassium on the salts of baryta, strontia, lime, or magnesia, the mellonides of barium, &c. are obtained as sparingly soluble salts, which crystallise in fine needles.

By boiling mellonide of potassium with excess of potash, ammonia is given off, and a new salt is formed. This decomposed by acetic acid, yields a white crystalline precipitate, containing no potash, probably a new acid. When dilute solution of mellonide of potassium is acted on by strong hydrochloric acid, and boiled till the hydromellonic acid is redissolved, the liquid, on cooling, deposits cyanuric acid, and contains sal ammoniac. Hydromellonic acid $Cy_3\,N\,H$, with 3 eq. of water $H_3\,O_3$, and 1 eq. oxygen, yields dry cyanuric acid, $Cy_3\,O_3$, and oxide of ammonium, $N\,H_4\,O$. The equivalent of oxygen is probably derived from the atmosphere; but this decomposition, as well as the preceding, requires minute investigation.

PRODUCTS OF THE DISTILLATION OF SULPHOCYANIDE OF AMMONIUM.

As an appendix to sulphocyanogen and its derivative mellone, we may consider the remarkable results of the action of heat on sulphocyanide of ammonium, $N\,H_4,\ C_2\,N\,S_2$.

When this salt is heated in a retort, there are given off as gases or vapours, bisulphuret of carbon, ammonia, and sulphuretted hydrogen, the two latter partly combined as sulphuret of ammonium:—

4 eq. Sulphocyanide of Ammonium . . may yield	$=C_8\ N_8\ S_8\ H_{16}$
2 eq. Bisulphuret of Carbon . .	$=C_2\ S_4$
4 eq. Ammonia	$=N_4\ H_{12}$
4 eq. Sulphuretted Hydrogen . .	$=S_4\ H_4$
1 eq. Mellone	$=C_6\ N_4$
	$C_8\ N_8\ S_8\ H_{16}$

Such is, in fact, the result of the action of a strong heat on the salt, mellone alone remaining in the retort. But if a more moderate heat be employed, a gray residue is left, containing the elements of mellone with those of ammonia. If this crude residue be dissolved in boiling potash, and the solution quickly filtered, there is deposited, on cooling, a heavy white powder, which is the chief product of the distillation of the sulphocyanide, in a state of purity. It has been called Melam, and its formula is $C_{12}\,N_{11}\,H_9 = 2\,C_6\,N_4 + 3\,N\,H_3$, or 2 eq. mellone and 3 eq. ammonia.

When the crude melam is acted on by oil of vitriol it dissolves with the aid of a gentle heat, and if water be added, and the whole boiled till the addition of carbonate of ammonia causes no further precipitate, the liquid, on cooling, deposits a large quantity of cyanuric acid, and is found to contain sulphate of ammonia. Now, as mellone, by the action of acids or alkalies, yields cyanuric acid and ammonia, it is easy to see that melam should do the same, $C_{12}\,N_{11}\,H_9$; that is, melam is equal to 2 eq. mellone $C_{12}\,N_8$, and 3 eq. ammonia $N_3\,H_9$; and if we represent mellone by $Cy_3\,N$, melam will be $2\,Cy_3\,N + 3\,N\,H_3$. Now let us add 12 eq. of water, and $2\,Cy_3\,N + H_{12}\,O_{12} = 2\,(Cy_3\,O_6,\,H_3) + 2\,N\,H_3$, and adding the 3 eq. of ammonia already present in melam, we have 2 eq. hydrated cyanuric acid, $2\,(Cy_3\,O_6,\,H_3)$, and 5 eq, ammonia, $5\,N\,H_3$, as the final results from 1 eq. melam and 12 eq. water, under the influence of acids and heat.

When melam is acted on by boiling with potash, a series of new compounds is obtained. The first is melamine, which is deposited in crystals when the alkaline solution cools. Melamine contains no oxygen, but is an artificial organic base, neutralising acids, and forming salts. Its formula is $C_6\,N_6\,H_6 = C_6\,N_4 + N_2\,H_6$; that is, it contains the elements of 1 eq. mellone, and 2 eq. ammonia.

The second new body is obtained as a white powder, when the alkaline solution which has deposited melamine, is supersaturated with acetic acid. It is called ammeline, and is also a base, although weaker than melamine. Its formula is $C_6\,N_5\,H_5\,O_2 = C_6\,N_4 + N\,H_3 + 2\,H\,O$, or 1 eq. mellone, 1 eq. ammonia, and 2 eq. water. It forms a crystallisable salt with nitric acid.

It may here be observed, that melam, $C_{12}\,N_{11}$, H_9, with 2 eq. water, $H_2\,O_2$, contains the elements of 1 eq. melamine, $C_6\,N_6\,H_6$, and 1 eq. ammeline. $C_6\,N_5\,H_5\,O_2$.

When either melamine or ammeline is dissolved in strong sulphuric acid, or melam in nitric acid, and the solution mixed first with two vol. of water, and then with four of alcohol, a white powder is obtained, resembling ammeline, but having the formula $C_{12}\,N_9\,H_9\,O_6 = 2\,C_6\,N_4 + N\,H_3 + 6\,H\,O$, or 2 eq. mellone, 1 eq. ammonia, and 6 eq. water. It is called ammelide, and has rather the characters of an acid than of a base.

Melamine, by the action of hydrochloric acid, aided by heat, is transformed into ammeline, giving off ammonia, while water is taken up. $C_6 N_6 H_6 + H_2 O_2 = C_6 N_6 H_8 O_2$, and $C_6 N_6 H_8 O_2 - N H_3 = C_6 N_5 H_5 O_2$.

Melam also, when treated in the same way, yields ammeline and ammonia. $C_{12} N_{11} H_9 + H_4 O_4 = C_{12} N_{11} H_{13} O_4$; and $C_{12} N_{11} H_{13} O_4 - N H_3 = C_{12} N_{10} H_{10} O_4 = 2 (C_6 N_5 H_5 O_2)$.

All these substances may be resolved, by the action of acids, into cyanuric acid and ammonia. It appears that they are all, that is, melam, melamine, and ammeline, first converted into ammelide, and that ammelide is the source of the cyanuric acid and ammonia.

It is obvious that they are all closely related to each other, and to cyanuric acid. That they are also related to mellone is probable, because when heated they leave a yellow residue, which is converted by a stronger heat into cyanogen and nitrogen; which, in short, is mellone. All these compounds may be represented as tribasic cyanurate of ammonia, minus water, or water and ammonia. Thus,

1 eq. anhydrous cyanurate of ammonia, $Cy_3 O_3, 3 N H_3 = C_6 N_6 H_9 O_3$
Minus 3 eq. water . . . . $= H_3 O_3$

Yields 1 eq. melamine . . . . . $= C_6 N_6 H_6$

1 eq. anhydrous cyanurate of ammonia . . . $= C_6 N_6 H_9 O_3$
Minus 1 eq. water $= H\ O$
„ 1 eq. ammonia $= H_3\ N$ } $N H_4 O$ . . $= N H_4 O$

Yields 1 eq. ammeline . . . . . $= C_6 N_5 H_5 O_2$

2 eq. anhydrous cyanurate of ammonia . . $= C_{12} N_{12} H_{18} O_6$
Minus 1 eq. ammonia $= N H_3$
„ 6 eq. water $= H_6 O_6$ } . . . $= N\ H_9\ O_6$

Yields 1 eq. melam . . . . $= C_{12} N_{11} H_9$

2 eq. anhydrous cyanurate of ammonia . . $= C_{12} N_{12} H_{18} O_6$
Minus 3 eq. ammonia . . . . . . $= N_3\ H_9$

Yields 1 eq. ammelide . . . . . $= C_{12} N_9\ H_9\ O_6$

When the mass remaining in the retort when urea is heated, and formerly believed to be cyanuric acid or cyanurate of ammonia, is acted on by acids, it yields cyanuric acid, and ammonia is found in the solution; but if it be boiled with water, an insoluble snow-white powder is obtained, which agrees with ammelide in almost all its properties. Its formula, however, is $C_6\,N_4\,H_4\,O_4$, and it may also be derived from cyanurate of ammonia, as follows:—

$$\begin{array}{lcr}
\left.\begin{array}{l}\text{1 eq. anhydrous tribasic cyanurate of ammonia,}\\ \qquad Cy_3\,O_3,\ 3\,N\,H_3\end{array}\right\} & = & C_6\,N_6\,H_9\,O_3 \\
\text{Minus 2 eq. ammonia} \quad . \quad . \quad . \quad . & = & N_2\,H_6 \\ \cline{3-3}
\qquad \text{and} & & C_6\,N_4\,H_3\,O_3 \\
\text{Plus 1 eq. water} \quad . \quad . \quad . \quad . \quad . \quad . \quad . & = & H\quad O \\ \cline{3-3}
\qquad \text{Yields 1 eq. of the new product from urea} & = & C_6\,N_4\,H_4\,O_4
\end{array}$$

This product, therefore, is intermediate between ammelide and cyanuric acid.

To be transformed into hydrated cyanuric acid, it has only to lose 1 eq. ammonia, and to gain 2 eq. water. Its formation from urea is very easily understood; for 4 eq. urea, minus 2 eq. carbonic acid and 4 eq. ammonia, will give this compound:—

$$\begin{array}{ll}
\text{4 eq. urea} \quad . \quad . \quad . \quad . \quad . & C_8\,N_8\,H_{16}\,O_8 \\
\left.\begin{array}{ll}\text{Minus 2 eq. carbonic acid } C_2\,O_4 & \\ \text{,, } \quad \text{4 eq. ammonia} & N_4\,H_{12}\end{array}\right\} & =C_2\,N_4\,H_{12}\,O_4 \\ \cline{2-2}
\text{1 eq. of the new compound} \quad . \quad . & C_6\,N_4\,H_4\,O_4
\end{array}$$

In order to render still more obvious the relation of these compounds, melam excepted, to cyanuric acid and among each other, let us express the hypothetical compound N H by M_2, M, therefore, standing for ½ eq. N H. We then have—

$$\begin{array}{lll}
\text{Cyanuric acid, } C_6\,N_3\,H_3\,O_6 \quad . \quad . & =Cy_3 & O_6+H_3 \\
\text{Melamine, } C_6\,N_6\,H_6 \quad . \quad . \quad . \quad . & =Cy_3 & M_6+H_3 \\
\text{Ammeline, } C_6\,N_5\,H_5\,O_2 \quad . \quad . \quad . & =Cy_3 & \left\{\begin{array}{l}M_4\\O_2\end{array}\right.+H_3 \\
\text{Ammelide, } C_6\,N_{4,}\,H_4\,O_3 \quad . \quad . \quad . & =Cy_3 & \left\{\begin{array}{l}M_3\\O_3\end{array}\right.+H_3 \\
\text{The new compound from urea, } C_6\,N_4\,H_4\,O_4 & =Cy_3 & \left\{\begin{array}{l}M_2\\O_4\end{array}\right.+H_3 \\
\text{And cyauuric acid} \quad . \quad . \quad . \quad . \quad . & =Cy_3 & O_6+H_3
\end{array}$$

Here we see the change in properties accompanying the gradual substitution of M for O. At one end of the series is melamine, a base, containing no oxygen; at the other, cyanuric acid, a highly oxygenised acid; while ammeline is a weak base, and the remaining two are neutral, or have a tendency, but a very slight one, to acid properties.

Before quitting these compounds, it is proper to point out that as sulphocyanic acid corresponds to cyanic acid, sulphur being substituted for oxygen, so sulphocyanide of ammonium corresponds precisely in the same way to urea; for urea is $C_2 N_2 H_4 O_2$, and sulphocyanide of ammonium is (see above) $C_2 N_2 H_4 S_2$. That this analogy is not imaginary we have seen in the similarity of the action of heat on both.

$$\begin{array}{lr}
\text{In the case of urea, 4 eq.} \quad . \quad . \quad . \quad . \quad . & =C_8 N_8 H_{16} O_8 \\
\left.\begin{array}{l}\text{yield 2 eq. carbonic acid, } C_2 O_4 \\ \text{and 4 eq. ammonia, } \quad N_4 H_{12}\end{array}\right\} \quad . \quad . & =C_2 N_4 H_{12} O_4 \\
\hline
\quad \text{Leaving 1 eq. of the new body} \quad . \quad . \quad . & =C_6 N_4 H_4 \ O_4
\end{array}$$

$$\begin{array}{lr}
\text{In the case of sulphocyanide of ammonium, 4 eq.} & =C_8 N_8 H_{16} S_8 \\
\left.\begin{array}{l}\text{yield 2 eq. bisulphuret of carbon, } C_2 S_4 \\ \text{and 4 eq. ammonia, } \quad N_4 H_{12}\end{array}\right\} & =C_2 N_4 H_{12} S_4 \\
\hline
\text{Leaving 1 eq. mellone + 4 eq. sulphuretted hydrogen} & =C_6 N_4 + H_4 S_4
\end{array}$$

The analogy only fails here in the fact, that the elements $C_6 N_4 H_4 S_4$, instead of uniting, as $C_6 N_4 H_4 O_4$ do, to form one compound, are resolved into two, namely, mellone and sulphuretted hydrogen. Of course the substance from urea may be viewed as compound of 1 eq. mellone and 4 of water; and it may possibly hereafter be resolved into those substances.

When mellone is boiled with nitric acid a new acid is formed, crystallising in octohedrons, which, when re-dissolved in water, form pearly scales. Liebig, who alone has studied it, found its formula and all its reactions exactly like those of cyanuric acid, and called it cyanilic acid: 1 eq. mellone and 6 eq. water, $C_6 N_4 + H_6 O_6$, are equal to 1 eq. cyanilic (or cyanuric) acid, and 1 eq. ammonia $(C_6 N_3 O_6, H_3) + N H_3$. Further experiments are required to establish cyanilic acid as an independent acid.

Sulphomellone. Hydrosulphomellonic acid.

According to the researches of Jamieson, which have reached me while this sheet was in proof, the orange-yellow powder, commonly called sulphocyanogen, and which, at p. 325, is said to contain 3 eq. of bisulphuret of cyanogen, 1 eq. hydrosulphocyanic acid, and 1 eq. water, really consists of the elements of 1 eq. of each of these three substances, $Cy\,S_2 + Cy\,S_2, H + HO = C_4\,N_2\,H_2\,O\,S_4$, how arranged we know not.

When dissolved to saturation in hydrosulphuret of sulphuret of potassium, KS, HS, the elements of 4 eq. sulphocyanogen, $4\,Cy\,S_2 = C_8\,N_4\,S_8$, along with 4 eq. of KS, HS, give rise to 7 eq. sulphuretted hydrogen, 7 HS; 1 eq. pentasulphuret of potassium KS_5; 2 eq. carbonate of potash, $2\,(KO, CO_2)$ and 1 eq. sulphomellonide of potassium, $C_6\,N_4\,H_3\,S_4, K$.

When this salt is decomposed by an acid, as hydrochloric acid, a simple exchange takes place. $C_6\,N_4\,H_3\,S_4\,K + H\,Cl = KCl + C_6\,N_4\,H_3\,S_4, H$. The latter formula represents the hydrosulphomellonic acid, which is a sparingly soluble white crystalline powder. It combines readily with the alkalies, and decomposes the carbonates of the alkaline earths when boiled with them. All the hydromellonides of the metals of the alkalies and alkaline earths are soluble and crystallize beautifully. The general formula for the anhydrous salts is $C_6\,N_4\,H_3\,S_4$, M; but the crystallized salts contain from 2 to 6 eqs. of water besides. The silver salt is anhydrous. The supposed radical of this acid, and of its salts, is not yet known in a separate state; but when the sulphomellonide of potassium is acted on by chlorine, there is separated a white powder, which seems to be sulphomellone, although Jamieson has not yet had time to ascertain that point. But the acid and its salts are rendered very simple by assuming the existence of this radical, which agrees with all the facts yet known, and makes the sulphomellonides analogous in composition, as they are in their relations, in their origin, and in their properties, to chlorides, bromides, iodides, fluorides, cyanides, and mellonides.

Having now concluded our sketch of the compounds derived from that of sulphur and cyanogen, it only remains to mention, that cyanogen forms one or two compounds with sulphuretted hydrogen, and that sulphocyanic acid forms a compound with the same gas. These compounds, however, are as yet too little known to permit of their being clearly laid down.

Cyanogen does not form any compound of importance with phosphorus or the remaining metalloids. But there is a very interesting and important series of compounds, in which we may conceive, with some probability, a radical to exist, formed of the elements of cyanogen and those of oxalyle (see p. 290), or carbonic oxide, $C_2 O_2$. This is the series of compounds derived from uric acid, and consequently closely connected with urea, which we have seen to be derived from cyanate of ammonia, and, through cyanic acid, from cyanuric acid, which connects it again with mellone, melam, and sulphocyanogen.

We shall first briefly describe the uric acid itself, as the starting point of an extensive series of products. The radical supposed to exist in these compounds will be better understood if described after we have become acquainted with them.

CYANOGEN WITH CARBONIC OXIDE.

XII. URYLE.

1. URIC ACID. $C_{10} N_4 H_4 O_6 = C_{10} N_4 H_3 O_5 + H O$.
Or $C_{10} N_4 H_2 O_4, 2 H O$; or $C_5 N_2 H O_2, H O$ (Bensch).

SYN. *Urilic Acid.—Lithic Acid.*—Occurs in small quantity in the healthy urine of man and quadrupeds, and in much larger quantity in the urine of birds, whether carnivorous or herbivorous, as in the pigeon and hawk tribes. In the urine of birds it forms the white part, in the form of urate of ammonia, and it is still found as such in guano—a substance produced by the long-continued action of the air on the urine (or excrement, for they are voided together) of sea-fowl. The only excrement of serpents, as, for example, of the boa constrictor, is a white semi-solid mass, which soon dries, and is pure acid urate of ammonia. In serpents, which are all carnivorous, it is very remarkable that the whole excreta (except occasionally hair and feathers, which pass undigested), should take the form of urate of ammonia. In diseased urine, uric acid is often deposited on cooling, and generally of a reddish colour; it also constitutes the most frequent form of gravel and of calculus, when deposited within the bladder. Acid urate of soda is found in the chalk stones of gouty patients; and it is well known that gout is a disease closely allied to calculus of this kind.

It is best obtained from the excrement (or urine) of the boa, which is powdered, and dissolved in 40 parts of boiling water by the gradual addition of caustic potash, till the liquid is decidedly alkaline. The uric acid forms urate of potash, which dissolves, while the ammonia escapes. The hot liquid, being filtered to separate impurities (and with the above proportion of water it filters rapidly, while with less it crystallises on the filter and chokes it up), is mixed with a decided excess of hydrochloric acid, when the uric acid is set free, and being insoluble, is deposited, at first, as a very bulky gelatinous hydrate, which in a few minutes spontaneously loses water and shrinks into a crystalline heavy precipitate. This is well washed with cold water and dried in the air, when it forms a shining powder, composed of distinct but minute crystals. If made from a cold saturated solution of urate of potash, the crystals are much larger, but contain 17·5 per cent.; in this case 4 eq. of water are expelled at 212°, leaving the same substance as that precipitated from a hot solution, which, when dried in the air, loses no weight at 212°. The latter is $C_{10} N_4 H_3 O_5 + H O = \overline{Ur} + H O$; the large crystals are a hydrate, $\overline{Ur}, H O + 4$ aq.

If pure white fragments of the urine of the boa have been used, the above simple process yields uric acid chemically pure, even when the solution in potash has had a decided yellow colour. This uric acid is snow white, and is entirely dissipated by heat, leaving no trace of ashes. But if the boa's urine have been impure, or if calculi have been employed to yield uric acid, in both of which cases the alkaline solution is brown, often very dark, and yields a coloured uric acid, or again if we wish to extract uric acid from guano, we must first purify the urate of potash by evaporating the alkaline solution till it crystallises in a mass, or passing carbonic acid through it to neutralise the free potash, when the acid urate of potash is deposited, and is washed on a filter with cold water, in which it is very sparingly soluble, till it is quite white. It is then dissolved in boiling water, and decomposed by hydrochloric acid as before. I have described thus minutely the preparation of pure and colourless uric acid, because none of the very interesting products derived from it can be obtained if we employ uric acid with even a very slight tinge of colour. The presence of a mere trace of the colouring matter of urine I have found to exert a most remarkable influence on the oxidation of uric acid by nitric acid, an influence which I can only compare to that of a ferment in causing a peculiar decomposition to take place.

Uric acid requires 15000 parts of cold and nearly 2000 of hot water for solution, and its solution reddens litmus. It forms salts with bases, especially with the alkalies and alkaline earths, all of which are insoluble or sparingly soluble.

The salts of uric acid have been lately examined by Bensch, according to whom the common urates are acid salts, while the eq. of the acid is only half that above given, or $C_5 N_2 H_2 O_3 = C_5 N_2 H O_2 + H O$. The neutral salts are $C_5 N_2 H O_2 + M O$, and the acid salts are $C_5 N_2 H O_2, M O + C_5 N_2$

HO_2, HO. Bensch has obtained the neutral salts of potash and soda, which are much more soluble than the well known urates of these bases, acid urates, according to Bensch. The neutral urate of potash dissolves in 35 parts of hot water, is alkaline, and is converted into the acid salt, both by water and carbonic acid. The acid salt requires 85 parts of boiling water for solution. The urates of soda are less soluble, and the acid urate of ammonia, the only salt formed with this base, dissolves in about 1600 parts of water at 60°, and 240 parts at 212°.

The only other urates hitherto examined by Bensch are the acid salts of magnesia, lime, baryta, strontia, lead, and copper. It would appear that, adopting his formula, the uric acid has a most remarkable tendency to form acid salts, and as it appears also to form double salts, it is not easy to see why he halves the formula of Liebig for the hydrated acid ; since the above characters are those which distinguish bibasic acids, and it would appear more consistent with the newly observed relations of the acid, to express the formula of Liebig, $C_{10}N_4H_4O_6 = C_{10}N_4H_3O_5 + HO$ by the following bibasic form $C_{10}N_4H_2O_4 + 2HO$ than by the monobasic form $2(C_5N_2HO_2, HO)$. If we adopt the bibasic formula, then the general formulæ for the neutral and acid salts as above given by Bensch, will become, respectively, $C_{10}N_4H_2O_4 + 2MO$, and $C_{10}N_4H_2O_4 + \left.\begin{matrix}MO\\HO\end{matrix}\right\}$.

PRODUCTS OF THE OXIDATION OF URIC ACID.

Uric acid is very permanent under ordinary circumstances, but is readily oxidised by powerful oxidising agents, such as peroxide of lead, peroxide of manganese, permanganate of potash, and nitric acid.

1. *Oxidation of uric acid by peroxide of lead.*—If uric acid be mixed with twenty parts of boiling water, and peroxide of lead added in small portions to the liquid kept boiling, the brown colour of the oxide disappears, and a heavy white powder is formed. When we have added about two parts of the oxide for one of uric acid, or, at all events, when the oxide begins not to lose its brown colour, the hot liquid is to be filtered, and on cooling it deposits a number of hard brilliant white crystals, of which more are obtained on evaporation. The mother liquid at last crystallises in a mass of very soluble prismatic crystals. These last are pure urea : the first crystals are Allantoine, and the powder is oxalate of lead, mixed with a little carbonate, and with the excess of peroxide. Hence, the

products of this oxidation are, Urea, Allantoine, and Oxalic Acid. After describing allantoine, we shall be able to explain the reaction.

Allantoine.—$C_4\ N_2\ H_3\ O_3$.—SYN. *Allantoic Acid.*—This body was first observed in the allantoic fluid of the fetal calf, which is, in fact, the urine of the fetal animal. When this fluid is evaporated, it deposits crystals of allantoine, formerly called allantoic acid, which, however, is not an acid. Its occurrence in the allantoic fluid—that is, as an ingredient in urine—and its artificial production from uric acid by a process of oxidation, are facts of very great interest when viewed in connection. It is best obtained from uric acid, as above described. It is a very indifferent, or neutral substance, and forms few compounds; only one, with oxide of silver, has been described, the formula of which is $C_8\ N_4\ H_5\ O_5 + Ag\ O = 2$ eq. allantoine, minus 1 eq. water, and plus 1 eq. oxide of silver.

When boiled with alkalies, it is resolved into ammonia which escapes, and oxalic acid which combines with the alkali. In fact, both allantoine, $C_4\ N_2 + H_3\ O_3$, and oxalate of ammonia, $C_2\ O_3 + N\ H_3$, may be represented as formed of cyanogen and water, and it is obvious that the addition of 3 eq. of water, to 1 eq. of allantoine gives $C_4\ N_2 + H_6\ O_6 = 2\ (C_2\ O_3 + N\ H_3)$.

We can now explain the formation of allantoine.

1 eq. Uric acid			$=C_{10}\ N_4\ H_4\ O_6$
Plus 2 eq. oxygen (from 2 eq. $Pb\ O_2$)	$=O_2$	$\left.\begin{matrix} \\ \end{matrix}\right\} H_3\ O_5 =$	$H_3\ O_5$
and 3 eq. water . .	$H_3\ O_3$		
Together			$=C_{10}\ N_4\ H_7\ O_{11}$
Are equal to 1 eq urea			$=C_2\ N_2\ H_4\ O_2$
2 eq. oxalic acid			$=C_4\ O_6$
1 eq. allantoine			$=C_4\ N_2\ H_3\ O_3$
Together			$=C_{10}\ N_4\ H_7\ O_{11}$

Or, in the form of an equation,

$$C_{10}N_4\ H_4\ O_6 + O_2 + H_3\ O_3 = C_2\ N_2\ H_4\ O_2 + 2\ C_2\ O_3 + C_4\ N_2\ H_3\ O_3.$$

That allantoine is closely related to uric acid and urea further appears from the fact, that 1 eq. uric acid, 1 eq. urea, and 1 eq. water, added together, are exactly equal to the sum of 3 eq. allantoine. $C_{10}\ N_4\ H_4\ O_6 + C_2\ N_2\ H_4\ O_2 + H\ O = C_{12}\ N_6\ H_9\ O_9 = 3\,(C_4\ N_2\ H_3 O_3)$.

2. *Oxidation of uric acid by peroxide of manganese.*—This is performed much as the preceding, and there appear to be produced compounds, partly the same as those from peroxide of lead, partly different. Of the latter, one at least is crystallisable, but has not been sufficiently examined. The subject requires investigation.

3. *By permanganate of potash.*—In this oxidation also, some products appear, which are obtained by peroxide of lead, such as urea ; and, in some forms of the experiment at all events, oxalic acid ; but I have also observed the formation of a new acid, containing nitrogen, the precise nature and composition of which is not yet ascertained.

4. *By nitric acid.*—This mode of oxidation of uric acid has been minutely studied by Liebig and Wöhler, and they have shown that it yields a very large number of new and important products, among which is again found urea, and also, under certain circumstances, oxalic acid. The changes are best traced when colourless nitric acid of a considerable concentration, of Sp. G. 1·45 for example, is employed.

1. *Alloxan.*—When uric acid is added, in small portions, to this acid, it is dissolved with a gentle and uniform effervescence, due to the escape of pure carbonic acid and nitrogen gases, without any trace of the red vapours of nitrous acid. Heat is also developed, so that no external heat is required, and it may even be necessary to moderate the reaction by placing the vessel in cold water. If too much uric acid be added at once, or if the mixture be allowed to get too hot, a violent reaction ensues, accompanied by copious red fumes, after which the experiment cannot succeed, and must be recommenced with fresh materials. The presence of a trace of the colouring matter of the urine infallibly causes this violent reaction, even with a much weaker nitric acid, and thus prevents us from obtaining the desired result, even to a small extent. In all these cases, the whole seems to be converted into oxalate and carbonate of ammonia. When the operation is properly managed, and a little practice makes it quite easy, there appear, in the warm liquid, after a certain quantity of uric acid has been dissolved, granular crystals of the new compound, alloxan. If more uric acid be added, it is still decomposed, and when the warm liquid (at about 120°) contains a great many crystals, it is allowed to cool, when the quantity of crystals greatly increases. They are now thrown on a filter stopped with asbestus, and when they have drained, the acid liquor still in their pores is displaced by a little ice-cold water, which is added till the droppings have only a slight acid taste.

The crystals are now dissolved on the funnel with water at 120°, and the filtered solution evaporated at that or even a lower temperature, till, on being set aside, it deposits large transparent crystals of hydrated alloxan, which are chemically pure. The mother liquid of these crystals, being gently evaporated, yields more, and the final mother liquid, which is now rather acid, from nitric acid, is added to the original acid mother liquor, to be used for other purposes. By the above process, I have constantly obtained, without difficulty, upwards of from 90 to 105 parts of hydrated alloxan, quite pure, from 100 of uric acid, besides what remains in the mother liquid, and cannot be extracted in that form. Not more than 2 oz. or 3 oz. of nitric acid should be used in one operation, and this quantity will decompose about one-third of its weight of uric acid, or more.

The crystals of hydrated alloxan, when heated to 212° lose about 27 per cent. of water, = 6 eq. The dry or anhydrous alloxan, which may also be obtained in crystals when a saturated solution is evaporated in a warm place, is composed of $C_8 N_2 H_4 O_{10}$, which explains its formation from uric acid; for $C_{10} N_4 H_4 O_6 + O_2 + H_4 O_4 = C_8 N_2 H_4 O_{10} + C_2 N_2 H_4 O_2$: that is, uric acid, *plus* 2 eq. oxygen and 4 eq. water, yields 1 eq. alloxan and 1 eq. urea.

The urea, when formed, is in contact with hyponitrous acid (derived from nitric acid by the separation of 2 eq. oxygen), and is immediately decomposed by it, yielding oxide of ammonium, which combines with some free nitric acid, carbonic acid, and nitrogen, which two last escape as gases. $C_4 N_2 H_4 O_2 + N O_3 = N H_4, O + 2 C O_2 + N_2$. At the end of the operation, therefore, the acid liquid, which has deposited crystals of alloxan, contains nothing but alloxan, nitrate of ammonia, and free nitric acid. We may therefore express the final result as follows: $C_{10} N_4 H_4 O_6 + 2 (H O, N O_5) + 2 H O = C_8 N_2 H_4 O_{10} + (N H_4 O, N O_5) + 2 C O_2 + N_2$.

Alloxan is very soluble in water, also in alcohol. Its solution stains the skin pink, and gives to it a heavy sickly odour. Its taste is peculiar and almost acidulous; but, although it reddens litmus, it has not the chemical characters of an acid. It is a very remarkable substance, from the numerous transformations which it undergoes, when subjected to the action of different re-agents.

By the action of soluble fixed alkalies, it is converted into a powerful acid, *alloxanic acid:* by the action of ammonia it yields another acid, *mykomelinic acid;* boiled with peroxide of lead, it is converted into *urea* and *carbonic acid;* by boiling with nitric acid it is changed into a new and powerful acid, *parabanic acid;* by the action of sulphuretted hydrogen and other deoxidising agents, it yields a new compound *alloxantine;* with hydrosulphuret of ammonia it gives a new salt called *dialurate of ammonia;* with sulphurous acid it combines, forming a compound acid, *alloxano-sulphurous* acid: and with sulphite of ammonia it forms another new salt called *thionurate of ammonia.* Such are the compounds formed by the direct action of re-agents on alloxan; but many others are produced by the action of re-agents on these, singly or jointly. Thus, when alloxan and alloxantine are both present in a hot solution, ammonia causes the development of a deep purple colour, and the deposition, on cooling, of the gold green crystals of *murexide;* acids acting on thionurate of ammonia produce *thionuric acid*, *uramile*, and *uramilic acid;* acids acting on murexide, produce *murexan;* acids acting on a dialurate of ammonia separate *dialuric acid;* ammonia, acting on parabanic acid, converts it into a new acid, *oxaluric acid;* and by the action of heat on alloxanate of baryta another new acid, *mesoxalic acid*, is produced. Alloxanic acid, when heated, yields *leucoturic acid* and *difluan;* and alloxantine when boiled with hydrochloric acid yields *alituric* and *dilituric acids.* We shall endeavour briefly to trace the formation and the relations of these remarkable products.

2. *Alloxanic Acid.*—Its formula $C_8 N_2 H_2 O_8 + 2 HO$. It is therefore isomeric with alloxan, and differs from it in this, that 2 eq. water have become basic, and replaceable by metallic oxides. It is a bibasic acid. It is formed when solution of alloxan is mixed with barytic water, as long as the white precipitate first formed redissolves with a gentle heat. When it begins to be permanent, a drop or two of alloxan is added to clear all up; and on cooling, alloxanate of baryta is deposited in small white crystals. From this salt the acid is obtained by adding sulphuric acid, so as to separate all the baryta. The acid solution on evaporating yields crystals of alloxanic acid. The acid, when neutralised by ammonia, forms, with nitrate of silver, a white precipitate, which, when boiled, becomes yellow, and is reduced with effervescence. When the solutions of its salts, with baryta, lime, and strontia, are boiled they become turbid, depositing carbonates, while urea and a mesoxalate remain dissolved. The formula of the neutral alloxanates is $C_8 N_2 H_2 O_8, 2 MO + aq.$; that of the acid salts is $C_8 N_2 H_2 O_8, \left.\begin{matrix} MO \\ HO \end{matrix}\right\}$.

Schlieper has lately studied the salts of alloxanic acid, and has confirmed the view above given. But he has also examined the products of decomposition of this acid, which are remarkable.

When a solution of alloxanic acid is boiled to dryness and pretty strongly heated in a capsule, carbonic acid is given off, and, when at last the residue ceases to yield any gas, and flows smoothly, the addition of water causes the separation of a crystalline powder in small quantity which is *leucoturic acid;* while the liquid contains a neutral body, *difluan.*

3. *Leucoturic Acid* is white and crystalline, sparingly soluble, and not decomposed by nitric acid. It is dissolved by ammonia, with which it forms a crystallisable salt, and by potash, which, however, soon transforms it into oxalic acid and ammonia. Its composition is $C_6 N_2 H_3 O_6 = C_6 N_2 H_2 O_5 + H O$. It contains the elements of 2 eq. cyanogen $C_4 N_2$, 1 eq. oxalic acid $C_2 O_3$, and 3 eq. water, $H_3 O_3$. With 3 more eqs. of water, it is resolved, when acted on by potash, into oxalic acid and ammonia.

$$C_6 N_2 H_3 O_6 + 3 H O = 2(N H_3) + 3(C_2 O_3).$$

4. *Difluan*, the more soluble product of the decomposition of alloxanic acid, is precipitated from the aqueous solution by absolute alcohol as a flocculent mass, which in vacuo dries up to a light bulky white powder, which, when exposed to the air, very rapidly deliquesces; hence its name. It is an indifferent body, which is dissolved by potash, and rapidly decomposed in contact with that base. Its composition is, $C_6 N_2 H_4 O_5$, thus containing 1 eq. of hydrogen more, and 1 eq. of oxygen less, than leucoturic acid. When it is resolved into oxalic acid and ammonia, oxygen is probably absorbed from the air, unless hydrogen be given off, or some other new product formed. Thus $C_6 N_2 H_4 O_5 + 2 H O + O_2 = 3 (C_2 O_3) + 2 (N H_3)$. This reaction has not been fully studied; but oxalic acid and ammonia are certainly produced.

Schlieper has observed a third product, along with leucoturic acid and difluan, which appears to contain 1 eq. of hydrogen more and 1 eq of oxygen less, than difluan. This, however, is not established, from the small amount of the substance obtained. The three formulæ exhibit the inverse variations in the hydrogen and oxygen.

Leucoturic acid . . .	$C_6 N_2 H_3 O_6$
Difluan	$C_6 N_4 H_4 O_5$
The third product . . .	$C_6 N_2 H_5 O_4$

The formation of leucoturic acid and of difluan from alloxanic acid is very simple.

1 eq. leucoturic acid . . .	$C_6 \; N_2 \; H_3 \; O_6$
1 eq. difluan	$C_6 \; N_2 \; H_4 \; O_5$
4 eq. carbonic acid	$C_4 \; O_8$
1 eq. water	HO
2 eq. alloxanic acid . . .	$C_{16} \; N_4 \; H_8 \; O_{20}$

5. *Hydurilic Acid.*—In the preparation of alloxan, Schleiper, on one occasion obtained a new body, which proved to be the ammonia salt of a new acid, hydurilic acid, $C_{12} \; N_3 \; H_5 \; O_{11}$. It is a bibasic acid, $= C_{12} \; N_3 \; H_3 \; O_9 + 2 \; H \; O$. It forms minute white prisms, sparingly soluble in cold water. It may be viewed as a compound of water and uryle ($C_8 \; N_2 \; O_4$), for $3 \; (C_8 \; N_2 \; O_4) + 10 \; H \; O = 2 \; (C_{12} \; N_3 \; H_5 \; O_{11})$. Hence its name.

It is evidently formed by an incomplete oxidation of uric acid, but Schlieper was not able to reproduce it.

With nitric acid, it yields a new acid, Nitrohydurilic acid, of very similar external character, the empirical formula of which seems to be, $C_8 \; N_3 \; H_2 \; O_{14}$. This is equal to

1 eq. Uryle	$C_8 \; N_2 \; O_4$
1 eq. Nitric Acid	$N \; O_5$
3 eq. Oxygen	O_3
2 eq. Water	$H_2 \; O_2$
	$C_8 \; N_3 \; H_2 \; O_{14}$

And it is formed from

2 eq. Hydurilic Acid (anhydrous) .	$C_{24} \; N_8 \; H_6 \; O_{18}$
3 eq. Nitric Acid	$N_3 \; O_{15}$
9 eq. Oxygen	O_9
3 eq. Nitrohydurilic Acid . . .	$C_{24} \; N_9 \; H_6 \; O_{42}$

Schlieper has further detected, in the same operation, in which he observed the hydurilic acid, another new acid, of which, however, little is known. Its empirical formula was found to be, $C_{10} \; N_2 \; H_5 \; O_9$. It has not been named.

6. *Mesoxalic Acid.*—Obtained, in combination with baryta, by boiling alloxanate of baryta; or combined with oxide of lead, by adding alloxan in solution, to a boiling solution of acetate of lead. The baryta salt is pale yellow, and sparingly soluble; the lead salt white and insoluble. The former is $C_3 \; O_4 \left\{ \begin{matrix} Ba \; O \\ H \; \; O, \end{matrix} \right.$

the latter $C_3O_4, 2PbO$. The acid may be obtained from either of these salts; it crystallises, is very sour, and is probably bibasic, and has, also probably, the formula $C_3O_4, 2HO$. In that case, the anhydrous acid is very remarkable as a new compound of carbon and oxygen, of the same class as mellitic and oxalic acids; hence the name. It is characterised by forming, when neutralised by ammonia with nitrate of silver, a yellow precipitate, which, when heated, is reduced with brisk effervescence. This is evidently the cause of the reaction of alloxanic acid, above mentioned, with nitrate of silver. Mesoxalic acid deserves and requires a very careful investigation. Its formation from alloxan or alloxanic acid, if its formula be C_3O_4, is very easily explained: for 1 eq. alloxan, *minus* 1 eq. urea, gives 2 eq. mesoxalic acid. $C_8N_2H_4O_{10} - C_2N_2H_4O_2 = C_6O_8 = 2C_3O_4$.

7. *Mykomelinic Acid*—$C_8N_4H_5O_5$.—is formed when ammonia acts on solution of alloxan; when a yellowish gelatinous precipitate of mykomelinate of ammonia soon appears. This boiled with dilute sulphuric acid yields a similar yellowish precipitate, which, when dry, forms a powder sparingly soluble in cold, more readily in hot, water. It is decidedly acid. It is formed of the acid by the reaction of 2 eq. of ammonia on 1 eq. alloxan. $C_8N_2H_4O_{10} + 2NH_3 = C_8N_4H_5O_5 + 5HO$. It would appear to differ from allantoine, only by 1 eq of water: for 2 eq. of allantoine are $C_8N_4H_6O_6$.

8. *Parabanic Acid*—$C_6N_2O_4 + 2HO$—is formed when alloxan or uric acid is heated with an excess of nitric acid, and the solution concentrated until on cooling it forms a soft crystalline mass. This is dried on a tile, and the dry crystals are purified by solution in hot water, filtration, and recrystallisation. A large quantity of parabanic acid may easily be obtained from the acid mother liquors of alloxan. When pure, the acid is beautifully white and crystallised, very acid, and very soluble. It is characterised by its great permanence in the free state, for it may be boiled with nitric acid, as its preparation shows, and at the same time by its extreme proneness to change in contact with bases. Thus, if neutralised with ammonia in the warm solution, it deposits, on cooling, a crystallised salt, which is oxalurate of ammonia. The same change takes place with all bases except oxide of silver, so that the parabanate of silver is the only salt of this very powerful and remarkable acid which can be obtained. To be converted into oxaluric acid, parabanic acid only requires 3 eq. of water. The production of parabanic acid is very simple. 1. From uric acid. $C_{10}N_4H_4O_6 + O_4$

$+ H_2 O_2 = C_2 N_2 H_4 O_2 + 2CO_2 + C_6 N_2 O_4, 2HO$
2 From alloxan. $C_8 N_2 H_4 O_{10} + O_2 = 2CO_2 + 2HO + C_6 N_2 O_4, 2HO$.

9. *Oxaluric Acid,*—$C_6 N_2 H_3 O_7 + HO$.—Formed by the action of bases on parabanic acid. $C_6 N_2 O_4 + KO + 3HO = C_6 N_2 H_3 O_7, KO$. The acid is obtained by adding dilute sulphuric acid to a hot saturated solution of oxalurate of ammonia, prepared by the action of ammonia on parabanic acid. On cooling, the oxaluric acid is deposited as a heavy white powder. When long boiled in water, it is decomposed into oxalate of urea and free oxalic acid. In fact, it contains the elements of 2 eq. oxalic acid and 1 eq. urea. $2 C_2 O_3 + C_2 N_2 H_4 O_2 = C_6 N_2 H_3 O_7, HO$. It is also characterised by forming with oxide of silver a white salt, which dissolves in hot water, and crystallises beautifully on cooling.

The *oxalurate of ammonia*—$NH_4 O + C_6 N_2 H_3 O_8$—is formed whenever a solution of alloxan, or alloxantine in water, or of uric acid in nitric acid, is evaporated with excess of ammonia, and where colouring matter is present, as when ammonia is made to act on the acid in the mother liquors of alloxan, the oxalurate is often deposited in radiated hemispherical concretions, which sometimes attain the size of an inch or two in diameter, and are very hard. When decolorised by animal charcoal, it forms small, soft, flexible needles. I have found that this salt, when exposed to heat in a retort, yields ammonia, hydrocyanic acid, and much oxamide, besides water, and perhaps other products, while a dark residue is left.

10. *Thionuric Acid*—$C_8 N_3 H_7 S_2 O_{14} = (C_8 N_4 H_5 O_8, 2SO_2) + 2HO$—is formed when sulphite of ammonia, with excess of base, is added to solution of alloxan, and the whole boiled for a few minutes, or until crystals appear in the hot liquid. On cooling it forms a semi-solid mass, from the separation of a large quantity of thionurate of ammonia in beautiful silvery crystals, which are to be washed with cold water, and dried on a tile. From this salt thionurate of lead is prepared, and this, being decomposed by sulphuric acid, yields thionuric acid. The acid is crystallisable, but very soluble. It is bibasic, and contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid, not however as such, for the elements of 2 eq. water have assumed the basic form.

Its most striking character is, that when its solution is heated it becomes turbid from the deposition of a new compound, uramile, and in the liquid *sulphuric* acid may now be found, which was not previously present. $C N_3 H_5 O_8 + 2SO_2 = C_8 N_3 H_5 O_6 + 2SO_3$; so that the sulphurous acid obtains oxygen from the rest of the acid, and becomes sulphuric acid, leaving uramile, $C_8 N_3 H_5 O_6$.

Thionurate of Ammonia—$(C\ \ N_3 H_5 O_8, 2 SO_3) + 2 NH_4 O + 2$ aq.—is formed as above-described. When its solution is mixed with 1 eq. of hydrochloric acid, half the ammonia is removed, and by evaporation we obtain *acid thionurate of ammonia* in minute silky needles. But when the hot solution of thionurate of ammonia is mixed with an excess of acid, the thionuric acid is set free and instantly decomposed, uramile being deposited. Little is known of the other thionurates.

11. *Uramile*, $C_8 N_3 H_5 O_6$.—Its formation has been described above. It occurs either as a crystalline powder, or in dendritic or feathery crystallisations, of very beautiful aspect. It dissolves in ammonia and potash, and the solution absorbs oxygen; becoming purple, and depositing green crystals of murexide, or of potassium-murexide. When boiled with peroxide of mercury, and a very little ammonia, it is also converted into murexide. Boiled with caustic potash, or with dilute acids, it is said to yield uramilic acid.—Nitric acid re-converts it into alloxan.

12. *Uramilic Acid*.—Obtained, by Liebig and Wöhler, by evaporating acid thionurate of ammonia, or uramile, with dilute sulphuric acid; also, it is said, by boiling uramile with potash. It appeared to these chemists as fine prisms, very soluble in water, and its analysis indicated the formula $C_{16} N_5 H_{10} O_{15}$; which might be derived from 2 eq. uramile by the loss of 1 eq. ammonia, and the addition of 3 eq. water. $2 (C_8 N_3 H_5 O_6) + 2 HO - NH_3 = C_{16} N_5 H_{10} O_{15}$. But this acid has not been again obtained, and its existence is still doubtful.

13. *Alloxantine*, $C_8 N_2 H_5 O_{10}$.—Obtained in large quantity by diluting the acid mother liquid of alloxan with 3 or 4 parts of water, and passing a current of sulphuretted hydrogen through it. In a short time sulphur is deposited, and then white crystals of alloxantine. When a large quantity has formed, it is collected with the sulphur, on a filter, washed with a little cold water, and the filter with its contents then boiled with a large quantity of water. The solution filtered while hot and with the addition of a few drops of hydrochloric acid, deposits, on cooling, a large crop of pure crystals of alloxantine. The acid liquid, filtered from the first deposit, often, on standing a day or two, deposits a large additional quantity of alloxantine. This always happens, if too much sulphuretted hydrogen has been used; for that converts the alloxantine partially into dialuric acid, which is more soluble, but by absorbing oxygen from the air, is reconverted into alloxantine, and thus deposited.

Alloxantine may also be obtained by deoxidising a pure solution of alloxan, either by sulphuretted hydrogen, or by other deoxidising agents ; or by heating a solution of alloxan to the boiling point, either by itself or with the addition of dilute mineral acids, when alloxantine is formed and deposited on cooling. But the process above given for converting into alloxantine the alloxan of the acid mother liquor, which cannot be purified by crystallisation, is so productive, and yields alloxantine so pure, that, if we have to prepare alloxan, we need never be at a loss for alloxantine.

The formation of alloxantine from alloxan by sulphuretted hydrogen is easily explained, for these compounds only differ by 1 eq. hydrogen, which the alloxan takes from sulphuretted hydrogen. Oxidising agents, by converting this hydrogen into water, readily reconvert alloxantine into alloxan. $C_8 N_2 H_5 O_{10} + O = HO + C_8 N_2 H_4 O_{10}$.

Alloxantine forms white, hard, brilliant crystals, which never exceed a certain small size. It is very sparingly soluble in cold water, much more so in hot water. Its solution is characterised by giving with solution of baryta a deep violet precipitate, which with excess of baryta, changes to white ; and by instantly reducing nitrate of silver, forming a black powder of silver, the alloxantine passing into alloxan, or oxaluric acid. The crystals of alloxantine, heated to 300°, lose 3 eq. of water.

In the preparation of alloxan, it is necessary, as has been stated, to be very careful that the first solution of the crystals formed in the nitric acid should not be heated too strongly, because, as this solution contains free nitric acid, alloxantine is formed at a certain temperature ; and besides, even a pure solution of alloxan, if boiled, is partly converted into alloxantine. The action of diluted nitric and other mineral acids on alloxan is to produce, from 2 eq. alloxan, 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid, the latter, with 3 eq. water, producing bicarbonate of ammonia. When solution of alloxan is boiled alone, it is converted into alloxantine, parabanic acid, and carbonic acid. $3 (C_8 N_2 H_4 O_{10}) = 2 (C_8 N_2 H_5 O_{10}) + C_6 N_2 H_2 O_6 + 2 CO_2$.

In all these, or in similar cases, the presence and the relative proportion of alloxantine contained in alloxan at any period, may be judged of by the colour of the precipitate formed in baryta. If pure white, no alloxantine is present : if slightly pink, it is present in small quantity ; if deep violet, all, or nearly all, the alloxan has been converted into alloxantine.

It is when both alloxan and alloxantine are present, that the addition of ammonia produces the deep purple colour, and the green crystals of murexide. When ammonia acts on alloxantine alone, it gives rise to uramile, and, finally, to oxalurate of ammonia.

One most remarkable change which alloxantine undergoes is that caused by the further action of sulphuretted hydrogen. If that gas be passed through a hot solution of alloxantine sulphur is precipitated, and an acid liquid is obtained, which, if neutralised by carbonate of ammonia, forms a salt in soft white silky crystals, the dialurate of ammonia. Alloxantine, by the action of hydrogen, which removes 1 eq. oxygen, is converted into dialuric acid.

14. *Dialuric Acid*, $C_8 N_2 H_3 O_7 + HO = C_8 N_2 H_4 O_8$—Produced by the action of sulphuretted hydrogen on alloxantine. $C_8 N_2 H_2 O_{10} + HS = S + 2 HO + C_8 N_2 H_4 O_8$. It is best obtained, in combination with ammonia, by adding a slight excess of hydrosulphuret of ammonia to a solution of alloxan or alloxantine, when a copious crystalline precipitate appears. This, when boiled, dissolves in the liquid, and on cooling is deposited in minute silky prisms, which are white, but in drying become pink or even deep red. They should be washed on the filter, first with diluted hydrosulphuret of ammonia, then with alcohol, to which a little hydrosulphuret has been added; and lastly, with pure alcohol; and dried by pressure in blotting-paper, and in the vacuum of the air-pump. They may thus be obtained white, or very nearly so; and when once quite dry, they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of dialuric acid are deposited on cooling. These crystals resemble somewhat those of alloxantine, but are larger, and not so brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed into alloxantine, from which dialuric acid only differs by 1 eq. oxygen and 1 eq. water.

Dialuric acid is a powerful acid. Its salts are insoluble or sparingly soluble, and only permanent in the dry state. The dialurate of ammonia, above described, is the most interesting.

15. *Alituric Acid.*—This acid is formed when alloxantine is boiled with hydrochloric acid, and was discovered by Schluper. It is soluble in 15 or 20 parts of hot water, and is deposited on cooling as a bulky crystalline powder. It is not altered by nitric acid. Its formula is $C_6 N_2 H_3 O_4 = C_6 N_2 H_2 O_3 + H O$. When heated with potash, ammonia is disengaged, and the addition of an acid causes a precipitate of a new body, apparently composed of $C_{18} N_5 H_8 O_{18} + K O$. Such a body might be formed from 3 eq. alituric acid + 4 eq. oxygen + 2 eq. water, the whole — 1 eq. ammonia.

16. *Dilituric Acid.*—This is found in the liquid obtained

when the preceding acid is purified from alloxantine by nitric acid, in combination with ammonia. The acid retains the ammonia with such force that it has not yet been obtained in a separate form. The ammoniacal salt is $C_8\,N_3\,H\,O_8 + N\,H_4\,O + H\,O$; and the acid is supposed to be bibasic, $C_8\,N_3\,H\,O_8 + 2\,H\,O$.

It is probably a coupled acid, for it contains the elements of 3 eq. cyanic acid, 2 eq. carbonic acid, and 3 eq. water. $3\,(C_2\,N\,O) + 2\,C\,O_2 + 3\,H\,O = C_8\,N_3\,H_3\,O_{10}$. The silver salt explodes when heated, which is rather favourable to this view.

17. *Murexide.* SYN. *Purpurate of Ammonia.*—Formed, as already mentioned, when ammonia acts on a solution containing both alloxan and alloxantine, which explains its production when ammonia is added to the solution of uric acid in dilute nitric acid, after evaporation to a certain extent: also, when uramile or murexan is boiled, with red oxide of mercury or oxide of silver, in water, with a few drops of ammonia, or when uramile or murexan is dissolved in ammonia and exposed to the atmosphere; and in a great variety of circumstances from all the preceding compounds, or nearly all of them.

On the small scale, 4 grains of alloxantine and 7 grains of hydrated alloxan, are dissolved together in $\frac{1}{2}$ oz. by measure of water by boiling, and the hot solution added to $\frac{1}{6}$ oz. by measure of a saturated or nearly saturated solution of carbonate of ammonia, the latter being cold. This mixture has exactly the proper temperature for the formation of murexide; and it does not, owing to its small bulk, remain too long hot. It instantly becomes intensely purple, while carbonic acid is expelled; and as soon as it begins to cool, the beautiful green and metallic-looking crystals of murexide appear. As soon as the liquid is cold, these may be collected, washed with a little cold water, and dried on filtering-paper. I have obtained them, by the above process, and on this small scale, of from 2 to 3 lines in length. When made with larger quantities, the crystals are always smaller, owing, probably, to some effect of the slower cooling of the larger mass of liquid, as continued heat is not favourable to their formation. If we do not care about having the finest crystals, we may prepare murexide in large quantity by adding solution of alloxan to a boiling solution of alloxantine, and cautiously adding cold solution of carbonate of ammonia, till the mixture has become nearly black, and the green crystals begin to appear. The vessel being removed from the fire, deposits a very large quantity of murexide. In these processes, the residual liquid is still coloured, and is alkaline from excess of ammonia: if kept, it loses the red colour, becomes yellowish, and if evaporated, yields much alloxanate of ammonia in crystals.

Murexide is one of the most beautiful products of chemistry: the crystals are metallic green by reflected light, like the cantharides fly or the gold beetle, and deep red by transmitted light. Their solution is deep purplish red, and they dissolve in potash with the most splendid purplish blue colour that can be imagined; this, however, soon disappears. When their solution is acted on by a dilute mineral acid, it is decolorised, and deposits a shining scaly crystalline powder, of a pale yellow colour, which is murexan. The same compound is obtained when acids are added to the solution of murexide in potash, after the purple tint has disappeared on digestion in a gentle heat.

The composition of murexide is uncertain, and there are different views of its constitution. According to some it is a salt of ammonia; and this view is supported by the fact that, with salts of baryta and oxides of lead and silver, it yields purple salts, which, according to Fritzsche, contain the same acid that in murexide is combined with ammonia, and which may be called purpuric acid. But murexide is not a compound of ammonia with the purpuric acid of Prout, for when that body (murexan) is dissolved in ammonia, it only forms murexide by absorbing oxygen from the air, and yields other compounds at the same time. Again, the action of sulphuretted hydrogen is inconsistent with the view of murexide being a salt of ammonia, and in many of its relations it more resembles a neutral body—such as a compound of amide. Its products of decomposition are very numerous, and altogether the subject is one of much difficulty. Possibly there may be two substances similar in appearance, but distinct in constitution; one a salt of ammonia, the other an indifferent body, or an amidide. The great discrepancy in the results of analysis, as obtained by Liebig and Wöhler on the one hand, and Fritzsche on the other, as well as some differences in the properties ascribed to it by different chemists, lead to some such conclusion. The formula considered by Liebig and Wöhler the most probable, all things considered, but not established, is $C_{12}\,N_3\,H_6\,O_8$; another somewhat less probable, is $C_{20}\,N_8\,H_{10}\,O_{14}$. Both of these will enable us to account for its production in different circumstances. The formula of Fritzsche, which agrees with his analysis, is $C_{16}\,N_6\,H_8\,O_{11} = N\,H_3 + C_{16}\,N_5\,H_5\,O_{11}$. The salt formed with nitrate of silver is, $C_{16}\,N_5\,H_5\,O_{11} + Ag\,O$, which would exhibit the unusual phenomenon of ammonia, instead of oxide of ammonium, being replaced by oxide of silver; and the baryta compound is $C_{16} N_5 H_5 O_{11} + HO + BaO$. Admitting the formulæ of Fritzsche for the silver and barium compounds to be correct, these are not demonstrated to be salts of purpuric acid; but besides this, his formula for murexide does not enable us to explain its production in any case. In these circumstances, we shall not attempt to explain the formation of murexide, further than to point out, that it appears to require the presence of a compound intermediate between alloxan and alloxantine (the former losing oxygen, the latter gaining it), and of ammonia: and that it is not the only product.

18. *Murexan.* SYN. *Purpuric Acid.* $C_6 N_2 H_4 O_5$?—Formed by the action of acids on murexide, but along with several other products. It appears as a shining powder, composed of scales, generally pale yellow, sometimes pale brown, never quite white. It is insoluble in water or nearly so, but the liquid filtered from it has always a peculiar opalescent aspect and play of colours. It dissolves in potash and ammonia, and the solutions become purple, by absorbing rapidly oxygen from the air, and finally deposit green crystals. When boiled with peroxide of mercury, water, and a little ammonia, it yields murexide. It dissolves in oil of vitriol, and is precipitated unchanged by water. In all these characters, except in its external aspect, it coincides entirely with uramile, and it is not impossible that it may be hereafter found to be uramile, disguised by the presence of a foreign substance. For the present, however, its analysis compels us to distinguish it from uramile.

Having now described the numerous products of the oxidation of uric acid by nitric acid, we are prepared to understand the nature of the radical supposed to be common to most of these compounds.

URYLE. $Ul. = C_8 N O_4 = 4 CO + 2 C_2 N.$

SYN. *Cyanoxalic Acid.*—This radical is unknown in the separate form. It contains the elements of four eq. carbonic oxide or 2 eq. oxalyle ($C_2 O_2$), and 2 eq. cyanogen. Hence the name cyanoxalic acid. Assuming it to exist, we have the following series :—

Rational formulæ.	Names.	Empirical formulæ.
Ul + 1 eq. urea	= Uric acid	$= C_{10} N_4 H_4 O_6$
$Ul + O + 5 HO$	= Alloxantine	$= C_8 N_2 H_5 O_{10}$
$Ul + O_2 + 4 HO$	= Alloxan	$= C_8 N_2 H_4 O_{10}$
$Ul + 4 HO$	= Dialuric acid	$= C_8 N_2 H_4 O_8$
$Ul_3 + 10 HO$	= Hydurilic acid	$= 2(C_{12} N_3 H_5 O_{11})$

Rational formulæ.		Names.		Empirical formulæ.
Ul $+ NO_5 + O_3$ $+ 2 HO$	=	Nitrohydurilic acid	=	$C_8 N_3 H_2 O_{14}$
Ul $+ NH_3 + 2 HO$	=	Uramile	=	$C_8 N_3 H_5 O_6$
Ul $+ O_2 + 4 HO$ $+ NH_3 + 2 SO_2$	=	Thionuric acid	=	$C_8 N_3 H_7 O_{14} S_2$

The ready conversion of these compounds one into another is a strong argument for the existence of the radical uryle. But the rational formulæ above given do not represent what we suppose to be the actual arrangement; they only point out by what simple means, as the addition or removal of oxygen, or ammonia, or water, the elements of the new compounds might be supplied. The other derivatives of uric acid are probably compounds of different radicals: thus, parabanic and oxaluric acids each contain only 6 eq. of carbon, and cannot therefore be compounds of uryle.

The above brief sketch of the products derived from uric acid, will serve to show the inexhaustible variety of new products, which one complex body may yield. Notwithstanding all that has been done, we must consider this subject as merely opened up, and a further prosecution of it will infallibly lead to many interesting and valuable results.

APPENDIX TO URIC ACID.

1. *Uric or Xanthic Oxide.*—This is a very rare ingredient of urinary calculi. Its formula is $C_5 N_2 H_2 O_2$, which, taken double, differs from uric acid only by 2 eq. oxygen. Hence its name of uric oxide. It is soluble in potash and precipitated by acids as a white powder. It dissolves in nitric acid, and the solution evaporated to dryness leaves a yellow residue; hence the name of xanthic oxide. It is said to occur in small quantities in some kinds of guano.

2. *Cystic Oxide,* $C_6 N H_6 O_4 S_2$.—Another very rare form of calculus. It dissolves both in acids and alkalies, and has the characters of an organic base, forming crystalline compounds with acids. It is remarkable from the large quantity of sulphur it contains.

3. *Guanine,* $C_{10} N_5 H_5 O_2$.—This compound has been discovered quite recently in guano by Unger, who at first supposed it to be identical with uric or xanthic oxide, but subsequently found it to be a distinct compound. It seems to be a base, somewhat analogous to urea; for it unites with hydrochloric, sulphuric, and nitric acids, forming crystallisable salts, among which are acid salts, with hydrochloric and nitric acids, a very rare phenomenon.

Guanine is a white powder, insoluble in water. Like other organic bases, it forms a double salt when its hydrochlorate is mixed with bichloride of platinum. This salt crystallises in fine orange yellow crystals, the formula of which is $(C_{10} N_5 H_5 O_2, H Cl) + 2 Pt Cl_2 + 4 H O$. It is remarkable that guanine forms no basic salts, as most weak bases do, but only neutral and acid salts.

Hyperuric Acid (?).—This acid was also discovered by Unger, who obtained it by acting on guanine with a mixture of hydrochloric acid and chlorate of potash. Its formula, according to Unger's experiments, is $C_{10} N_4 H_5 O_9$, which differs from uric acid by 1 eq. water, and 2 eq. oxygen; hence the name. Unger conjectures it, from the analysis of the silver salt, to be bibasic $C_{10} N_4 H_3 O_7 + 2 H O$; but the want of material has prevented him from fully investigating this curious acid; and he marks its formula, and even its name as doubtful.

The acid forms short rhombic prisms, colourless, and of brilliant lustre. When heated, it yields hydrated cyanic acid, water, and a residue of carbon. This might occur with the formula above given, for $C_{10} N_4 H_5 O_9 = 4 (C_2 N O, H O) + H O + C_2$.

XIII. BENZOYLE. $Bz = C_{14} H_5 O_2$.

This is the radical of Benzoic Acid, of oil of bitter almonds, and of an extensive series of compounds. The radical is not yet known with certainty in the separate form, although a compound exists, having the same composition. (See *Benzile.*) We shall describe first the benzoic acid, and afterwards the other compounds derived from, or connected with it.

1. Benzoic Acid. $C_{14} H_5 O_3, H O = Bz O, H O$, or $Bz O_2, H$.

This acid is found in gum benzoin, mixed with some resins; and it also occurs in the urine of herbivorous animals, under certain circumstances. It is also formed by the oxidation of the oil of bitter almonds. It may be obtained from benzoin by sublimation, the powdered gum being gently heated on an iron plate forming the bottom of a broad and short cylinder, the top of which is covered with bibulous paper pasted tightly down to the sides, while another cylinder slides over the upper end of the first, to prevent the escape of the acid. The vapours of the acid, which is very volatile, pass through the paper, and forming crystals, are there retained, falling on its upper surface. The following method, however, is far more productive, as in the process of sublimation some of the acid is always decomposed. Benzoin is dissolved in strong alcohol, and to the hot solution there is added hydrochloric acid in quantity sufficient to precipitate the resin: the whole is then distilled. The benzoic acid passes over under the form of benzoic ether (benzoate of oxide of ethyle); and when the greater part of the liquid has been distilled off, water is added to the residue, and distilled as long as any ether passes over with it. When this ceases, the hot water remaining in the retort is filtered, and on cooling deposits part of the benzoic acid in crystals. The benzoic ether and all the distilled liquors are now treated with caustic potash, until all the ether is decomposed, and the solution, now containing benzoate of potash, is heated to boiling, and supersaturated with hydrochloric acid. On cooling it deposits the benzoic acid in crystals. By this means the whole benzoic acid of the benzoin is obtained.

Benzoic acid forms fine light prismatic crystals, or flexible pearly scales. When pure, it has no smell, but by heat it acquires the odour of benzoin or of vanilla, and as commonly prepared it has a very pleasant odour derived from the presence of some foreign compound which accompanies the acid, and is not easily separated from it. It is very fusible and volatile, and its vapours are very irritating, provoking cough. It is inflammable, burning with smoke. It is sparingly soluble in cold water, more so in boiling water; it dissolves also in alcohol and ether.

With bases it forms salts, many of which are crystallisable. Their general formula is $Bz\ O, M\ O$, or $Bz\ O_2, M$. When the alkaline and earthy benzoates are heated in close vessels, they yield carbonates, while new products distil over, such as benzone, benzole, naphthaline, &c. The benzoate of peroxide of iron, $3\ Bz\ O + Fe_2\ O_3$, has a reddish white colour, and is insoluble. Benzoic acid, in the form of benzoate of ammonia, is therefore sometimes used as a means of separating peroxide of iron from some other bases. But its use requires many precautions, and it is quite inapplicable if alumina, glucina, yttria, or zirconia be present. Benzoate of silver, $Bz\ O, Ag\ O$, is sparingly soluble, and when formed in hot solutions crystallises on cooling.

2. Hyduret of Benzoyle. $C_{14}\ H_6\ O_2 = Bz\ H$.

Syn. *Essential oil of bitter almonds.*—When bitter almonds, after being macerated with water for a day or two, are distilled with the water, there is obtained a fragrant oily liquid, heavier than water, which contains, besides hyduret of benzoyle, benzoic acid, hydrocyanic acid, and benzoine, a solid compound isomeric with the hyduret of benzoyle. To purify it, this oily liquid is distilled along with a mixture of protochloride of iron and slaked lime, which retain the two acids, and the benzoine remaining behind, the pure hyduret passes over.

It is a colourless transparent liquid, of a high refractive power. It has a peculiar and very powerful smell, and it is on this account that the crude oil is so much used in perfumery. Its odour has been compared to that of hydrocyanic acid, but this has arisen from the fact that the crude oil contains both: for on comparing the two, no similarity can be perceived. It ought, however, to be borne in mind that the commercial oil is highly poisonous, not only because it contains hydrocyanic acid, but because the hyduret of benzoyle is poisonous. Hyduret of benzoyle boils at 356°.

When exposed to the air, it absorbs 2 eq. of oxygen, and is converted into pure crystallised benzoic acid. $Bz\,H + O_2 = Bz\,O, H\,O$. Heated with caustic potash in close vessels, it yields benzoate of potash and hydrogen gas, which is disengaged. $K\,O,\ H\,O + Bz\,H = K\,O,\ Bz\,O + H$. It is still more easily converted into benzoate of potash by an alcoholic solution of potash; the alcohol here swims above the salt, and holds in solution an oily matter not yet examined.

When hyduret of benzoyle is mixed with a little hydrocyanic acid, and placed in contact with aqua potassæ, lime water, or baryta water, it is gradually converted into the solid crystalline compound, isomeric with itself, which is called benzoine. When mixed with aqua ammoniæ, and gently heated, it produces a new compound, hydrobenzamide. With chlorine and bromine, if dry, it yields chloride and bromide of benzoyle, with hydrochloric and hydrobromic acids; if water be present, benzoic acid is likewise formed, part of which combines with some unchanged hyduret of benzoyle.

3. *Chloride of benzoyle*, formed by the action of dry chlorine on the hyduret, is a colourless liquid, of a strong disagreeable odour. It is formed as follows: $Bz\,H = Cl_2 = Bz\,Cl + H\,Cl$. With the alkalies it yields benzoate of the alkali, and chloride of the metal: $Bz\,Cl + 2\,K\,O = K\,O,\ Bz\,O + K\,Cl$. With dry ammonia it yields *benzamide;* with alcohol it produces benzoic ether and hydrochloric acid. $Ae\,O,\ H\,O + Bz\,Cl = Ae\,O,\ Bz\,O + H\,Cl$. When acted on by metallic bromides, iodides, sulphurets, or cyanides, it produces metallic chlorides, and bromide, iodide, sulphuret or cyanide of benzoyle. The *bromide of benzoyle* is a crystalline solid, in other respects analogous to the

chloride. The *iodide* and *sulphuret* of benzoyle are also crystallisable: the cyanide is a liquid having an odour like that of cinnamon.

4. Benzamide. $C_{14}\,N\,H_7\,O_2 = C_{14}\,H_5\,O_2 + N\,H_2 = Bz\,Ad.$

This compound is formed when dry ammonia acts on chloride of benzoyle, $Bz\,Cl + N\,H_2,\,H = Bz,\,N\,H_2 + H\,Cl$: also when hippuric acid (which see), is boiled with peroxide of lead. When prepared from the chloride, it is accompanied by sal ammoniac, formed by the hydrochloric acid produced, with the excess of ammonia. This is removed by cold water; and the benzamide, being dissolved in hot water, crystallises on cooling. It forms fine soft needles or pearly scales, very fusible and volatile. Like other amidides, it yields ammonia when boiled with alkalies, while a benzoate is formed.

5. Formobenzoilic Acid. $\left\{ \begin{array}{l} C_2\,H\,O_3 + C_{14}\,H_6\,O_2 + H\,O = Fo\,O_3, \\ \quad Bz\,H + H\,O. \end{array} \right.$

This compound is obtained by adding to distilled water some crude oil of bitter almonds, which always contains hydrocyanic acid (see *Amygdaline*), and evaporating to dryness along with some hydrochloric acid. From the dry mass, ether dissolves the new acid, which it deposits as a crystalline powder by evaporation. In this process, the hydrocyanic acid, under the influence of hydrochloric acid, is converted, along with the elements of water, into formic acid and ammonia. The latter combines with the hydrocyanic acid, the former with the hyduret of benzoyle, yielding formobenzoilic acid. With bases this acid forms salts, in which the quantity of base neutralized is exactly that which would be neutralized by the formic acid alone. Their formula is $M\,O + Fo\,O_3,\ Bz\,H$; by which it is seen that the hyduret of benzoyle has entered into the radical of the acid, without altering its power of saturation; and perhaps the rational formula of the acid ought rather to be, $(Fo\,O_4,\ Bz\,H) + H$; and that of the salts, $(Fo\,O_4,\ Bz\,H) + M$; which exhibits this view still more clearly.

6. Benzoate of Hyduret of Benzoyle. $C_{42}\,H_{18}\,O_8 = Bz\,O,\,HO + 2\,Bz\,H.$

This compound is formed when moist chlorine is passed through the oil of bitter almonds. Hydrated benzoic acid is formed, which unites with the unchanged hyduret. The action of moist chlorine in producing hydrated benzoic acid is as follows: $Bz\,H + 2\,H\,O + Cl_2 = 2\,H\,Cl + Bz\,O, H\,O$. The new compound is crystalline, insoluble in water, soluble in alcohol and ether. It is volatile without decomposition. An alcoholic solution of potash dissolves it, and converts it into benzoate of potash.

7. Hippuric Acid. $C_{18}\,N\,H_8\,O_5 + H\,O$.

This acid is found in very considerable quantity in the urine of herbivorous animals, such as the horse and cow, more especially when stall-fed. It has also been lately discovered by Liebig in human urine. It is easily obtained by evaporating gently to a small bulk the fresh urine of the horse or cow, and acidulating with hydrochloric acid. On standing, the liquid deposits brown crystals of hippuric acid, which may be decolorised by a little bleaching liquor and hydrochloric acid.

The pure acid forms pretty large semi-opaque four-sided prisms, sparingly soluble in cold water, very soluble in hot water, and in alcohol. When heated, it melts, and gives off benzoic acid, benzoate of ammonia, and an oily matter, which has a very fragrant odour like that of the tonka bean. By nitric acid it is converted into benzoic acid. Heated with peroxide of manganese and sulphuric acid, it yields ammonia, carbonic acid, and benzoic acid; boiled with peroxide of lead, it yields benzamide and carbonic acid.

With bases it forms salts, most of which are soluble and crystallisable.

Hippuric acid may be viewed in two ways; first, as a compound of benzamide with an acid, $C_4\,H\,O_3$ (fumaric or aconitic acid?) and it is remarkable that Schwarz, who has lately studied the hippurates, observed a very great similarity to the fumarates; as if the hyduret of benzoyle were simply taken up into the molecule of these salts, without much affecting their properties; secondly, as composed of hyduret of benzoyle, hydrocyanic acid, and formic acid. Either view readily accounts for its easy decomposition into benzoic acid and other products. As an ingredient of the urine, this acid is important; and we shall hereafter see that benzoic acid, taken into the system, appears in the urine as hippuric acid.

Dessaignes has recently shown, that, when hippuric acid is boiled with stronger acids for some time, it is decomposed, and yields benzoic acid, which crystallises on cooling; while the mother liquid, on further evaporation, yields fine crystals of the salts formed by the combination of sugar of gelatine (see *Gelatine*), with the acid employed. In fact, sugar of gelatine, according to Dessaignes, is a basis quite analogous to urea; and its salts, with the mineral acids, form double salts, and appear to act as acids, which is also the case with urea. If to

Hippuric acid	$C_{18}\,N_2\,H_9\,O_6$
We add 2 eq. water	$H_2\,O_2$
	$C_{18}\,N_2\,H_{11}\,O_8$
And from the sum deduct 1 eq. hydrated benzoic acid	$C_{14}\,H_6\,O_4$
There remains	$C_4\,N_2\,H_5\,O_4$

And this is the formula which Gerhardt has recently proposed for sugar of gelatine. Whether this formula, however, or those of Mulder and Boussingault, be preferable, it is certain that the salts, obtained as above, by Dessaignes, with nitric, hydrochloric, and sulphuric acids, are not distinguishable from those made with sugar of gelatine prepared from gelatine. Moreover, the sugar itself, separated from these salts, was found identical in properties with that from gelatine. The analysis of the sugar produced by the new method, which seems to be very pure, will no doubt settle the question as to the true formula of sugar of gelatine.

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZOYLE.

1. Hyposulphobenzoic Acid. $C_{14}\,H_4\,O_3 + S_2\,O_5 + 2\,H\,O$.

A bibasic acid. Formed when anhydrous sulphuric acid acts on crystallised benzoic acid $C_{14}\,H_5\,O_3, H\,O + 2\,S\,O_3 = C_{14}\,H_4\,O_3 + S_2\,O_5 + 2\,H\,O$. The acid is soluble and crystallisable, and forms with baryta a soluble and crystallisable salt, from which the acid may be obtained by the action of sulphuric acid. It forms two series of salts, one with 2 eq. of fixed base, the other with 1 eq. of fixed base and 1 eq. of water.

2. Bromobenzoic Acid. $C_{28}\,H_9\,Br\,O_8 + 2\,H\,O$.

A bibasic acid. When the vapour of bromine is allowed to act on benzoate of silver at the ordinary temperature, there is produced this acid, along with bromide of silver and hydrobromic acid. 2 eq. of benzoate of silver and 4 eq. of bromine yield 1 eq. bromobenzoic acid, 1 eq. hydrobromic acid, and 2 eq. bromide of silver. $2\,(C_{14}\,H_5\,O_3\,Ag\,O) + Br_4 = C_{28}\,H_9\,Br\,O_8 + H\,Br + 2\,Ag\,Br$. Ether dissolves the acid and deposits it on evaporation, in a confused mass of crystals, very sparingly soluble in water. When the acid crystallises, it takes up

2 eq. of water. With bases it forms salts, which are generally soluble and crystallisable. Their general formula is $C_{28}H_9BrO_8, 2MO$.

3. Benzole. $C_{12}H_6$.

SYN. *Benzine. Benzène. Phène.*—Occurs in the volatile liquids condensed from oil gas; but is best obtained in a state of purity by distilling 1 part of crystallised benzoic acid with 3 of slaked lime. It is a limpid, colourless liquid, of an agreeable etherial odour. Its Sp. G. is 0·85; it boils at 186°, and at 32° it becomes solid. It is insoluble in water, soluble in alcohol and ether. In its formation, 1 eq. of benzoic acid yields 2 eq. carbonic acid and 1 eq. benzole, the carbonic acid uniting with the lime, $C_{14}H_5O_3, HO = C_{12}H_6 + 2CO_2$. 4. *Sulphobenzide*, $C_{12}H_5SO_2$.—When anhydrous sulphuric acid acts on benzole, a viscid mass is formed, from which, by the addition of water, is separated a new compound, which may be dissolved and crystallised by means of ether. $C_{12}H_6 + SO_3 = HO + C_{12}H_5, SO_2$. Sulphobenzide is quite neutral. 5. *Hyposulphobenzidic Acid.*—This acid is found in the liquid from which the preceding compound has been deposited. Its formula is $C_{12}H_5, S_2O_5, + O$. It may be viewed as formed by the action of 2 eq. of dry sulphuric acid on 1 eq. of benzole, $C_{12}H_6 + 2SO_3 = C_{12}H_5, S_2O_5, HO$; or as formed by the combination of sulphobenzide with oil of vitriol, $C_{12}H_5, SO_2 + HO, SO_3$. Either view readily explains its formation. The acid is best obtained pure from its salt with oxide of copper (which crystallises very easily), by the action of sulphuretted hydrogen. It is very soluble, and may be crystallised. It has a very acid taste, and neutralises bases, forming crystallisable salts. 6. *Nitrobenzide*, $C_{12}H_5NO_4$. Syn. *Nitrobenzole.*—Formed when benzole is dissolved to saturation in fuming nitric acid, and water added to the hot solution. On cooling, the nitrobenzide falls to the bottom as a heavy oil. It is, at 60°, a yellow liquid, very sweet to the taste, with an odour like that of cinnamon; it boils at 434°, and solidifies at 37°. Its Sp. G. is 1·209. It is insoluble in water, soluble in alcohol and ether. It is formed from 1 eq. benzole and 1 eq. nitric acid, $C_{12}H_6 + NO_5 = HO + C_{12}H_5, NO_4$. By the action of reducing agents, such as sulphuretted hydrogen, nitrobenzide loses the whole of its oxygen, and, taking up 2 eqs. of hydrogen, it is transformed into aniline, $C_{12}NH_7$. (See *Aniline*). Nitrobenzide may be viewed as benzole, $C_{12}H_6$, in which 1 eq. hydrogen is replaced by nitrous acid, $C_{12}\left.\begin{matrix}H_5\\NO_4\end{matrix}\right\}$ while in aniline this eq. of hydrogen is replaced by amide; $C_{12}H_7N = C_{12}\left.\begin{matrix}H_5\\NH_2\end{matrix}\right\}$. By the further action of nitric acid, nitrobenzide is converted into dinitrobenzol, $C_{12}H_4N_2O_8 = C_{12}\left.\begin{matrix}H_4\\2\,NO_4\end{matrix}\right\}$ in which a second eq. of hydrogen is replaced by nitrous acid. This compound, acted on by hydrosulphuret of ammonia, yields nitroaniline, a base, the formula of which is $C_{12}\left.\begin{matrix}H_6\\NO_4\end{matrix}\right\}N$, corresponding to aniline $C_{12}H_7N$. 7. *Azobenzide,* $C_{12}H_5N$.—This compound is formed when an alcoholic solution of nitrobenzide is distilled with dry hydrate of potash. After the alcohol has distilled, the azobenzide volatilises, forming large red crystals, fusible at 150°, boiling at 380°. In the production of this compound alcohol takes a part, and there are formed, besides azobenzide, aniline, water, and oxalic acid, which remains combined with the potash. $2\,(C_{12}H_5NO_4) + C_4H_6O_2 = C_{12}H_5N + C_{12}H_7N + C_2O_3 + 3\,HO$. 8. *Chloride of benzole,* $C_{12}H_6Cl_6$.—Formed when chlorine gas and benzole are exposed to the sun's rays. It is a colourless crystalline solid. 9. *Chlorobenzine,* $C_{12}H_3Cl_3$.—Obtained by distilling the preceding compound with hydrate of lime, as a colourless oily liquid.—Bromine forms with benzole analogous compounds.

10. Benzone. $C_{13}H_5O$.

One of the products of the distillation of neutral benzoate of lime. When purified from benzole and naphthaline, it is an oily viscid colourless liquid, heavier than water. It differs from 1 eq. of anhydrous benzoic acid by 1 eq. of carbonic acid, $C_{14}H_5O_3 = C_{13}H_5O + CO_2$.

11. Hydrobenzamide. $C_{42}H_{18}N_2$.

When 1 vol. hyduret of benzoyle and 20 vol. of strong aqua ammoniæ are exposed in an hermetically sealed vessel to a temperature of from 105° to 120°, it is converted after a time into a crystalline mass, which is to be washed with ether. The residue dissolved in alcohol, yields, by spontaneous evaporation, regular crystals of hydrobenzamide. In its formation, 3 eq. hyduret of benzole, and 2 eq. ammonia, produce 1 eq. hydrobenzamide and 6 eq. water. $3\,(C_{14}H_6O_2) + 2\,NH_3 = C_{42}H_{18}N_2 + 6\,HO$. If, in preparing this substance, we employ the crude oil of bitter almonds, we obtain a yellow resinous mass, which is a mixture of *hydrobenzamide, benzhydramide, azobenzoyle,* and *azotide of benzoyle,* all of them discovered by Laurent. 12. *Benzhydramide* is isomeric with hydrobenzamide, but is not converted, like the former, into hyduret of benzoyle and sal ammoniac by the action of hydrochloric acid. 13. *Azobenzoyle*, $C_{42} H_{15} N_2$, is much less soluble in alcohol than the preceding. It is derived from benzoyle as follows:—$3 (C_{14} H_5 O_2) + 2 N H_3 = C_{42} H_{15} N_2 + 6 H O$. 14. *Azotide of benzoyle*, $C_{14} H_5 N$, is quite insoluble in boiling alcohol. It may be derived from anhydrous benzoic acid as follows:—$C_{14} H_5 O_3 + N H_3 = C_{14} H_5 N + 3 H O$.

15. Benzostilbine. $C_{31} H_{11} O_2$.

Rochleder has shown that when hydrobenzamide is heated with fused potash, till the mass begins to blacken, three new substances are formed; namely, a yellow oil in very small quantity, and two solid crystalline compounds, Benzostilbine and Benzolone. Benzostilbine is best obtained by heating only till the mass becomes like gamboge. It is then purified by solution in alcohol, which dissolves it readily when the yellow oil is present. When the oil is destroyed by a little chlorine, the benzostilbine is immediately deposited in small colourless crystals of silvery lustre, which are insoluble in water, sparingly soluble in alcohol, and soluble with a blood-red colour in oil of vitriol, from which water precipitates it unchanged.

16. Benzolone. $C_{11} H_4 O$.

This compound is formed in greatest quantity when the mixture of hydrobenzamide with potash is heated till it becomes blackish brown. The mass is then washed with water, and dissolved in oil of vitriol, to which it gives a splendid red colour. The addition of weak alcohol now causes the benzolone to separate in small crystals.

It is obvious that the two preceding compounds contain the whole carbon of the hydrobenzamide, without any of its nitrogen, and they may both be derived from it by the addition of 3 eq. of water and the elimination of 2 eq. ammonia,

1 eq. hydrobenzamide . . .	$C_{42} H_{18} N_2$
3 eq. water	$H_3 O_3$
	$C_{42} H_{21} N_2 O_3$
may yield	
1 eq. benzostilbine . . .	$C_{31} H_{11} O_2$
1 eq. benzolone	$C_{21} H_4 O$
2 eq. ammonia	$H_4 N_2$
	$C_{42} H_{21} N_2 O_3$

It would appear, however, that benzolone is also formed from benzostilbine, which is first produced, and then decomposed by the increased heat. Benzostilbine in fact contains the elements of 2 eq. benzolone, with an excess of carbon and hydrogen, which are partly given off in the form of carburetted hydrogen, and hydrogen, water also being decomposed, the oxygen of which combines with part of the carbon to form carbonic acid, which combines with the potash.

15. Amarine. $C_{42} H_{18} N_2$.

When the hyduret of benzoyle, or rather, the oil of bitter almonds, is acted on by ammonia and alcohol, there is found an organic base, to which Laurent, its discoverer, has given the name of *amarine.* Its formula is $C_{42} H_{18} N_2$, and it is, therefore, isomeric, or polymeric, with hydrobenzamide. It is a well-marked base, and we shall return to it as such.

16. Lophine. $C_{46} H_{16} N_3$.

When hydrobenzamide is subjected to the action of heat in close vessels, there is formed, among other products, a new organic base, which Laurent has named *lophine.* It has distinct basic properties, and will be again referred to in the section on organic bases. Its formula is $C_{46} H_{16} N_3$.

The formation of this and of the preceding compound is very interesting, as proving the derivation of bodies having the high atomic weight of the organic bases from bodies of lower equivalents; these bodies, as well as the isomeric hydrobenzamide and benzhydramide, being all derived from the hyduret of benzoyle, $C_{14} H_6 O_2$. There may be some doubt as to the atomic weight of indifferent bodies, such as hydrobenzamide; but there is hardly any as to that of the bases above mentioned, which are evidently formed by the coalescence of 3 or more eqs. of the hyduret of benzoyle, since 1 eqs. contains 42 or 46 eqs. of carbon, while the hyduret only contains 14 eqs. of that element.

17. Benzimide. $C_{28} N H_{11} O_4$.

According to Laurent, this compound is found in the crude oil of bitter almonds. It is crystallisable, and appears to be decomposed by acids into benzoic acid and ammonia. It may be derived from anhydrous bibenzoate of ammonia by the separation of 2 eq. water. $C_{28} H_{10} O_6 + N H_3 = C_{28} H_{11} N O_4 + 2 H O$. But this is not probable. A compound precisely similar is obtained when an alcoholic solution of potash is added to a mixture of hyduret of benzoyle and strong hydrocyanic acid; but this compound yields with acids ammonia and hyduret of benzoyle.

18. Benzoine. $C_{28} H_{12} O_4$.

Polymeric with hyduret of benzoyle. It is formed when an alcoholic solution of potash, or sulphuret or cyanide of potassium, act on the crude oil of bitter almonds, containing hydrocyanic acid. It separates in a congeries of small crystals, insoluble in water, soluble in alcohol. It may be volatilised without change. Sulphuric acid dissolves it with a violet colour. Hydrate of potash, melted with it, forms benzoate of potash, with disengagement of hydrogen. It dissolves with a violet colour in a hot alcoholic solution of potash, and is converted by boiling with it into benzilic acid. When its vapour is passed through a red-hot tube, it is converted into hyduret of benzoyle, or at least into an oil smelling like that compound, and passing into benzoic acid on exposure to the air. By the action of chlorine it loses hydrogen, and is converted into *Benzile*, a compound having the composition of the radical benzoyle.

The action of hydrocyanic acid in promoting the formation of benzoine is not yet explained; but it is certain that from pure hyduret of benzoyle we cannot procure it, while the addition of hydrocyanic acid ensures its formation. It is, probably, formed by the simple coalescence of 2 eqs. hyduret of benzoyle, and the derivatives of benzoine most likely agree with it in containing 28 eqs. of carbon.

19. Hydrobenzoinamide.

SYN. *Benzoinamide.*—Isomeric, or polymeric with hydrobenzamide. It is formed by exposing a mixture of benzoine and ammonia to a moderate heat; and appears as a white tasteless powder, volatile without decomposition.

20. Benzoinam. $C_{56} N_2 H_{24} O_2$.

When a mixture of ammonia, alcohol, and benzoine, is left for several months in a closed bottle, there are formed many products, among which are the preceding compound, benzoinamide, and a new substance, *benzoinam*, which is with difficulty purified. It forms small white needles, the formula of which is $C_{56} N_2 H_{24} O_2$. It is evidently formed by the coalescence of 2 eq. benzoine (itself produced by the coalescence of 2 eq. hyduret of benzoyle) while ammonia is taken up, and water separated. Thus 2 eq. benzoine $= C_{56} H_{24} O_8$, *plus* 2 eq.

ammonia $N_2\ H_6$, and *minus* 6 eq. water, $H_6\ O_6$, are equal to $C_{56}\ N_2\ H_{24}\ O_2$.

Benzoinam dissolves in acids, and is precipitated by alkalies; it seems, therefore, to have the characters of a weak base.

21. Benzile. $C_{28}\ H_{10}\ O_4$.

SYN. *Benzoyle.*—It is formed by the action of chlorine gas on melted benzoine. When cold the mass is boiled with alcohol, which on cooling deposits benzile in crystals, which are yellow six-sided prisms; insoluble in water, soluble in alcohol and ether, melting at 195° and volatile without decomposition. An alcoholic solution of potash dissolves it with a violet colour, and converts it into benzilic acid. Benzile has the composition in 100 parts of the supposed radical Benzoyle, but there is good reason to believe its equivalent to be twice as high.

22. Benzilic Acid. $C_{28}\ H_{11}\ O_5 + H\ O$.

Formed when benzile or benzoine is dissolved in a hot alcoholic solution of potash, and boiled until the violet colour at first produced has disappeared, and is no longer restored by a fresh portion of potash. To the boiling solution of benzilate of potash hydrochloric acid is added in excess, and on cooling the benzilic acid is deposited in colourless brilliant crystals, fusible at 248°, not volatile, but yielding, when heated, benzoic acid, and purple vapours. Sulphuric acid dissolves it with a bright crimson colour. Its formation is explained as follows:—1 eq. of benzile takes up 2 eqs. of water, one of which is incorporated in the acid; while the other is replaceable by bases. $C_{28}\ H_{10}\ O_4 + 2\ H\ O = C_{28}\ H_{11}\ O_5 + H\ O$. *Benzilate of potash* forms large transparent crystals, soluble in water and alcohol.

23. *Azobenzoide*—$C_{84}\ H_{33}\ N_5$? Obtained by adding ammonia to the oil produced when bitter almonds are distilled per descensum, and dissolving away by means of ether all other products. A white powder, decomposed by heat. Its formula is doubtful.

24. *Cyanobenzile.*—Formed when an alcoholic solution of benzile is warmed with $\frac{1}{3}$ of its volume of concentrated hydrocyanic acid. It is deposited in large transparent crystals, the composition of which is not yet known.

25. Hyduret of Sulphobenzoyle. $C_{14}\ H_5\ S_2,\ H$.

One vol. of crude essence of bitter almonds is dissolved in 8 or 10 of alcohol, and gradually mixed with 1 vol. of hydrosulphuret of ammonia. After a time, the mixture deposits a fine white powder, formed of grains smaller than those of starch, which give to the fingers a very persistent odour of garlic. It is insoluble in water and alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hyduret of a new radical, in which the oxygen of benzoyle has been replaced by sulphur. When heated, it melts, and if now allowed to cool, forms first a transparent plastic mass, and afterwards a brittle glass. If kept melted for some time, it crystallises, but is now altered.

26. Stilbene. $C_{28}H_{12}$.

When the preceding compound is strongly heated, it gives off a large quantity of sulphuretted hydrogen, and a little of a liquid, apparently bisulphuret of carbon. Continuing the heat, there distil over, first a substance crystallising in pearly scales, *stilbene ;* and later, a compound, crystallising in needles, called by Laurent, the discoverer, *sulphessale.* To obtain the stilbene pure, the first crystals are dissolved in boiling alcohol, which leaves undissolved the other body, and on cooling deposits stilbene in tables. These being dissolved in hot ether, form, by slow evaporation, remarkably fine crystals, with the pearly lustre of stilbite, hence the name. It is fusible and volatile, and combines with chlorine and bromine. Nitric acid decomposes it, giving rise to several new products. Chromic acid attacks it with violence, and reproduces hyduret of benzoyle.

Chloride of stilbene is formed when chlorine is passed through melted stilbene. It appears in two isomeric modifications, *a* and *b*, both of which have the formula $C_{28}H_{12}, Cl_2$, but crystallise in different forms. By the action of a boiling alcoholic solution of potash, each loses 1 eq. of hydrochloric acid (or its elements), and thus they produce two isomeric modifications of a new compound $C_{28}\left\{\begin{matrix}H_{11}\\Cl,\end{matrix}\right.$ which Laurent calls Chlostilbase; and in which 1 eq. of hydrogen of stilbene is replaced by chlorine. One of these is called Chlostilbase *a*, the other Chlostilbase *b*. Both are oily liquids, but they are distinguished by the action of bromine, which combines with both, producing again two isomeric compounds, both crystallisable, but in entirely different forms. Their formulæ are, $a\,C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right.+Br_2$ and $b\,C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right.+Br_2$.

Along with chloride of stilbene is formed another compound, chloride of chlostilbase, analogous to these bromides of chlostilbase. It is a crystallisable solid: formula, $C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right.+Cl_2$.

Bromide combines with stilbene, forming the bromide of stilbene, $C_{28} H_{12}, Br_2$, which is a white powder.

When stilbene is boiled with nitric acid, it forms several compounds not yet fully examined. Among these are Nitrostilbase, Nitrostilbèse, and Nitrostilbic acid. The latter, according to Laurent, is $C_{28} H_{11} NO_{14}$.

27. *Hyduret of Sulphazobenzoyle*, $(C_{14} H_5 S_{\frac{4}{3}} N_{\frac{2}{3}}) H$, or rather $C_{42} H_{15} S_4 N_2$, is generally formed along with hyduret of sulphobenzoyle. It seems to be hyduret of benzoile, in which the 2 eqs. oxygen of the benzoyle are replaced partly by sulphur, partly by nitrogen. Besides these compounds, Laurent has described a hydrosulphuret of azobenzoile, with the strange formula $C_{14} H_6 S N_{\frac{3}{4}}$. Ought it not rather to be $C_{14} H_6 SN$, or $C_{56} H_{24} S_4 N_3$?

28. Nitrobenzoic Acid. $C_{14} H_4 N O_7, H O$.

Formed when nitric acid acts on benzoic acid. It is a crystalline volatile acid, and contains the elements of benzoic acid, in which 1 eq. hyponitric or nitrous acid has been substituted for 1 eq. hydrogen. $C_{14} H_5 O_3 - H + N O_4 = C_{14} \left\{ \begin{matrix} H_4 \\ N O_4 \end{matrix} \right. O_3$; and the basic water of the benzoic acid unites with the new acid as with the old.

29. Bromide of Benzole. $C_{12} H_6 Br_6$.

This compound is formed as a white insoluble powder, when bromine acts on benzole. An alcoholic solution of potash removes hydrobromic acid (or its elements), and causes the separation of a white crystalline body, $C_{12} \left\{ \begin{matrix} H_3 \\ Br_3 \end{matrix} \right.$, which Laurent calls *bromobenzinise;* and which is formed by substitution of bromine for half the hydrogen of benzole. The bromide of benzole may, therefore, be $C_{12} \left\{ \begin{matrix} H_3 \\ Br_3 \end{matrix} \right. + 3 H Br$.

30. *Hydrocyanate of benzoine.*—$C_{46} N_2 H_{18} O_4$, is formed as a light crystalline matter, when oil of bitter almonds is mixed with one-fourth its volume of dry hydrocyanic acid, and warmed with its own volume of aqua potassæ, Sp. G. 1·25, diluted with six parts of alcohol. It arises from the action of 3 eqs. hyduret of benzoyle and 2 eqs. hydrocyanic acid: $3 (C_{14} H_6 O_2) + 2 (C_2 N H) = C_{46} N_2 H_{18} O_4 + 2 HO$.

31. *Hydrocyanate of benzile*, $C_{14} H_5 O_2 + C_2 NH = C_{16} NH_6 O_2$, is formed by direct combination when a hot alcoholic solution of benzile is mixed with an equal bulk of anhydrous hydrocyanic acid. It forms large colourless crystals.

Possibly the body called Cyanobenzile mentioned above, No. 24, may be identical with this compound.

The above is but a brief and imperfect notice of the numerous compounds which have been obtained from oil of bitter almonds by the various transformations and decompositions above mentioned. Probably no substance has yielded so rich a harvest of discovery as this remarkable oil, and for our knowledge of the new products we are indebted to Liebig and Wöhler, Mitscherlich, Zinin, Rochleder, but above all, to Laurent, who has discovered by far the greater part of them. Unfortunately, the very able researches of this indefatigable chemist are scattered in several different journals, many of them published at long intervals of time, and have nowhere been collected or exhibited to the world in a connected form. I have not been able to consult nearly all of the original papers, the references to which are very unsatisfactory; and I am consequently compelled to rest satisfied with the imperfect notices which I could find. The above list does not, I believe, contain even the names of several compounds belonging to this series, recently described by Laurent, of which I can procure no distinct account. The reader is therefore, of necessity, referred for the details of these remarkable investigations to the original memoirs which are to be found in the Annales de Chémie et de Physique, and the Journal de Pharmacie, besides several other French journals.

The study of these compounds has shed great light, and will, in future, shed much more, on the origin of the more complex organic molecules. In several instances, we see 2 or 3 eqs. of hyduret of benzoyle coalescing to yield 1 eq. of a new and more complex substance, either with or without a change in the relative proportion of oxygen and hydrogen, and with or without the addition of nitrogen. According to Laurent, compounds exist in which 4, 6, and even 9 eqs. of the hyduret have coalesced.

It was mentioned, in a former part of this work, that our power of artificially forming bodies which occur as products of organic life, was limited chiefly to the decomposition or splitting up of complex molecules, such as those of sugar, salicine, uric acid, or fibrine, into less complex molecules.

But, although this is still true of the actual products of organic life which have been imitated in the laboratory, the facts above described, show, that, under certain circumstances, we can, from the less complex molecules, build up more complex ones, so as to produce, if not the actual products of organic life, yet substances, entirely analogous to them, and equally complex.

Thus, the artificial bases, amarine, lophine, and benzoinam, have equivalents as high as those of the vegetable alkalies, morphia and quinine; and we have almost demonstrative evidence that these three compounds arise from the reverse process to that which yields urea, formic, oxalic, and salicylic acids. The latter are obtained by processes of *oxidation*, which tend to split up the more complex molecules into less complex ones: the former are, on the contrary, built up out of the less complex molecules, by processes of *reduction*. There are other cases, of recent discovery, which establish the same principle.

Now we know, that the distinguishing feature of vegetable life is the power of *reduction* possessed by plants, which easily deprive carbonic acid of its oxygen, an operation requiring a prodigious chemical force.

We are, therefore, warranted in concluding that we shall, in time, succeed, by means of the various processes of reduction known to chemists, (and possibly of new methods also), in producing, for example, the vegetable alkalies, morphine, quinine, and strychnine.

This consideration gives to the compounds of the Benzoyle series, and their derivatives, a high degree of interest, far surpassing that which would attach to them as a mere list of new compounds, each possessing a distinct composition and distinct properties.

Appendix to Benzoyle.

1. Amygdaline. $C_{40}NH_{27}O_{22}$.

Is found in bitter almonds, in the leaves of the cherry laurel, and probably in the kernels of all the bitter species of amygdalus and prunus, as the peach and plum. To obtain it, bitter almonds are pounded and forcibly pressed between warm iron plates to remove the fat oil (oil of almonds). The marc or residue is boiled with alcohol of 94 per cent., and the tinctures distilled off in the water-bath to the consistence of syrup. This liquid, which contains amygdaline and sugar, is diluted with water, mixed with yeast, and set aside. When the fermentation is over, the whole is filtered, and again evaporated to a syrup, which being mixed with a large excess of cold alcohol (of 94 per cent.) deposits the amygdaline as a white crystalline powder. This is pressed in folds of bibulous paper, and finally purified by repeated crystallisation from boiling alcohol. It forms crystalline scales very soluble in water, very sparingly soluble in cold alcohol, but more soluble in hot alcohol. It has a bitter taste. When heated it emits an odour like that of May blossom, and leaves a bulky coal.

When distilled with nitric acid, or other oxidising agents, it is resolved into ammonia, hyduret of benzoyle, benzoic acid, formic acid, and carbonic acid. Caustic alkalies convert it into ammonia and amygdalinic acid: permanganate of potash converts it into cyanate and benzoate of potash.

2. Amygdalinic Acid. $C_{40} H_{26} O_{24} + HO$.

Prepared by boiling amygdaline with baryta as long as ammonia is given off, and then removing the baryta from the soluble amygdalinate of that base by sulphuric acid. By evaporation it yields a transparent amorphous mass, which has a very pleasant acid taste. Nitric acid, and other oxidising agents, convert it into hyduret of benzoyle, with formic and benzoic acid. Its salts are almost all soluble: their formula is $C_{40} H_{26} O_{24} + M O$.

3. Distilled Water of Bitter Almonds.

Expressed bitter almonds are made into a thin cream with water, and this distilled in the heat of a chloride of calcium bath, till a quantity of water has passed over equal in weight to the almonds before being pressed. The distilled water is milky from suspended oil of bitter almonds, and smells both of hyduret of benzoyle and of hydrocyanic acid. When freshly prepared, it contains little more than 1 grain of hydrocyanic acid per ounce; but its strength diminishes by keeping, and as it is difficult to obtain it of uniform strength even when fresh, it is not a good form of administering hydrocyanic acid. It is remarkable, that nitrate of silver does not detect the hydrocyanic acid, unless ammonia is added with the nitrate, and after a time neutralised by nitric acid. It is used in medicine, especially on the Continent, and is poisonous.

4. Laurel Water.

Obtained by distilling two parts of fresh leaves of *prunus laurocerasus* with water till three parts have passed over. It exactly resembles the preceding water, and is equally uncertain, and equally poisonous.

THEORY OF THE FORMATION OF HYDURET OF BENZOYLE FROM BITTER ALMONDS.

Bitter almonds contain, like sweet almonds, a large quantity of an albuminous or caseous matter, called *emulsine* or *synaptase*, along with abundance of a mild fat oil, the oil of almonds, very similar to olive oil. But in addition to these, the bitter almonds contain 4 or 5 per cent. of amygdaline, which is not present in sweet almonds.

Now, if the amygdaline be removed by boiling alcohol, the residue, when distilled with water, does not yield a trace of the volatile oil of bitter almonds. Again, if the residue of the bitter almonds, after the fat oil has been pressed out, be heated to such a point as to coagulate the emulsine, before water is added, the distillation also yields no volatile oil, even although the amygdaline be present.

These facts prove that the production of the volatile oil of bitter almonds depends on the presence, first, of amygdaline; secondly, of soluble emulsine; and that is the result of the mutual action of these bodies on each other. This is further demonstrated by the fact, that if amygdaline be placed in contact with the emulsine or synaptase of *sweet almonds*, and water, distillation of the mixture now yields the oil abundantly.

When the solution of 10 parts of amygdaline in 100 of water is added to a solution of 1 part of synaptase in 10 of water, mutual decomposition at once takes place: the liquid acquires the odour of hyduret of benzoyle and of hydrocyanic acid, and when distilled, yields the crude oil of bitter almonds, which is a mixture of these two compounds. The residue of the distillation contains sugar in such quantity, that it is probable the elements of the synaptase have contributed to form it; and when this sugar is destroyed by fermentation, a fixed acid is found. If the synaptase has been coagulated, it has not the slightest action on amygdaline.

When the expressed bitter almonds are moistened with water, the very same reaction occurs; and if enough water be present to dissolve the oil as it is formed, the whole amygdaline disappears in a short time. But if the expressed almonds be thrown into boiling water, the synaptase coagulates, and can then produce no change in the amygdaline. To obtain the full proportion of oil, 1 part of expressed almonds should be macerated for 24 hours with 20 parts of water at about 102°, and then distilled.

100 parts of amygdaline produce 47 of crude oil, and these 47 parts of crude oil contain almost exactly 6 of anhydrous hydrocyanic acid; so that 17 grains of amygdaline dissolved in 1 oz. of emulsion of *sweet* almonds, yields a mixture containing 1 grain of dry hydrocyanic acid, and consequently of the same strength as the distilled water professes to be. This mixture has, besides, the advantage of containing the hyduret of benzoyle present in the distilled water, to which is perhaps owing the superiority of the distilled water of bitter almonds on laurel leaves over mere diluted hydrocyanic acid, a superi-

ority which, according to the Continental physicians, is very decided and obvious. The above simple recipe, given by Liebig and Wöhler, is admirably adapted for extemporaneous use, and the mixture ought never to be made in a larger quantity at a time, as, like the distilled water, it alters by keeping.

In the above remarkable decomposition, we have a very beautiful example of a metamorphosis in which the elements of two bodies take a share; but as the whole of the products are not yet exactly known, and even the composition of the emulsine or synaptase is uncertain, we cannot explain the whole change with precision. We know, however, that from 1 eq. amygdaline, $C_{40}\ NH_{27}\ O_{22}$, the following compounds may be derived:—

1 eq. hydrocyanic acid	$C_2\ \ NH$
2 eqs. hyduret of benzoyle . . .	$C_{28}\ \ H_{12}\ O_4$
½ eq. sugar	$C_6\ \ H_5\ O_5$
2 eqs. formic acid	$C_4\ \ H_2\ O_6$
7 eqs. water	$H_7\ O_7$
1 eq. amygdaline	$C_{40}\ NH_{27}\ O_{22}$

Also, 1 eq. amygdalinic acid, $C_{40}\ H_{26}\ O_{24}$, may yield:—

3 eqs. formic acid	$C_6\ H_3\ O_9$
2 eqs. hyduret of benzoyle . . .	$C_{28}\ H_{12}\ O_4$
½ eq. sugar	$C_6\ H_5\ O_5$
6 eqs. water	$H_6\ O_6$
1 eq. amygdalinic acid	$C_{40}\ H_{26}\ O_{24}$

Now, we can trace all these products among the results of this transformation; and, it is probable, not only that there is more sugar than can be accounted for by the amygdaline, but also that other products, not yet known, are formed: as, for example, the fixed acid above alluded to. The emulsine or synaptase, which produces this remarkable change in amygdaline, in which it itself participates, contains nitrogen, is soluble in water, coagulable by heat, and in short very analogous both to albumen and caseine, along with which we shall again notice it. In the almond it appears to be accompanied by albumen.

We have seen, above, that the assumption of the existence of the radical benzoyle brings a number of compounds into a more easily understood form, and very materially aids the memory by enabling us to classify these compounds as analogous to others better known. Other views may be taken of this series of compounds: for example, according to Dumas, hyduret of benzoyle may be represented as a compound of benzoic acid with a carbo-hydrogen: $2\,C_{14} H_5 O_3 + (C_{14} H_5) H_3$: benzoic acid being the teroxide and the carbo-hydrogen the terhyduret of the body, $C_{14} H_5$: for $2\,(C_{14} H_5) O_3 + (C_{14} H_5) H_3 = C_{42} H_{18} O_6 = 3\,(C_{14} H_6 O_2) = 3\,Bz\,H$. The same view might be extended to some of the other compounds of benzoyle, but it is complex, and cannot well be applied to benzamide, hydrobenzamide, and several others. Again, according to Mitscherlich, benzoic acid is $C_{12} H_6 + 2\,C\,O_2$; that is, benzole plus 2 eqs. carbonic acid; while a dry benzoate would contain, united to the base, the hypothetical body *benzide*, $C_{12} H_5$, and the equally hypothetical anhydrous oxalic acid, $C_2 O_3$. These views appear both to be in all respects inferior to that which we have adopted, and which must be retained, until a better shall be proposed. If I understand rightly some expressions in a recent paper by Laurent, that chemist considers hyduret of benzoyle, $C_{14} H_6 O_{21}$ as the oxide of a radical *benzene;* but it does not appear, whether it is $(C_{14} H_6) + O_2$ or $(C_{14} H_6 O) + O$. The term oxide of benzene, however, may be applied to one of the isomeric modifications of the hyduret.

XIV. Salicyle. $C_{14} H_5 O_4 = Sa$.

This is the hypothetical radical of a remarkable series of compounds; and, as such, belongs to the same group as benzoyle. Its most interesting compound is the hyduret of salicyle, which we shall therefore first consider.

1. Hyduret of Salicyle. $C_{14} H_5 O_4, H = Sa\,H$.

Syn. *Salicylous acid.*—This compound is found as the chief ingredient in the essence of meadowsweet, that is, the essential oil obtained by distilling the flowers of *spiræa ulmaria* with water. It is probable that, like the essence of bitter almonds, it is formed by the metamorphosis of a compound or compounds present in the flowers. The crude essence is distilled with aqua potassæ, which combines with the hyduret, and an oil distils over which seems to be a carbohydrogen. The salt of potash being now redistilled with a slight excess of dilute sulphuric acid, yields the pure hyduret of salicyle.

It may also be obtained by distilling one part of salicine, one part of bichromate of potash, two and a half of oil of vitriol, and twenty of water, together. The salicine is dissolved in part of the water, and the acid diluted with the rest. The mixture is then made in a retort, and after the effervescence which takes place is over, the whole is distilled, and yields the hyduret, to the amount of one-fourth of the salicine employed.

Hyduret of salicyle is an oily colourless liquid, having a fragrant aromatic odour and a burning taste. Its Sp. G. is 1·1731, and it boils about 380°. With chlorine and bromine it forms new compounds. With bases it forms salicylurets, water being separated. $HSa + MO = HO + MSa$, so that it has the characters of an acid.

Salicyluret of ammonium, Sa, NH_4, is formed when concentrated ammonia is poured upon hyduret of salicyle. It is a yellow solid, having a faint odour of roses. When moist, this salt is decomposed spontaneously, becoming black, and giving off ammonia and an odour like that of roses. With dry ammoniacal gas, hyduret of salicyle forms the compound $3\ Sa\ H + 2\ NH_3$.

Salicylimide, $C_{42}\,N_2\,H_{18}\,O_6$, is formed when caustic ammonia is added, drop by drop, to a solution of 1 vol. hyduret of salicyle in 3 vol. alcohol, and the small yellow crystals which first formed are dissolved by a gentle heat. On standing, salicylimide appears in the form of golden yellow brilliant prisms. It is formed from 3 eqs. hyduret of salicyle and 2 eqs. of ammonia, by the separation of 6 eqs. water, $3\,(C_{14}\,H_6\,O_4) + 2\ NH_3 - 6\ HO = C_{42}\,N_2\,H_{18}\,O_6$. As it is no longer soluble in the liquid from which it was first deposited, it is probable that the yellow salt first formed, which dissolved in the alcohol by aid of a gentle heat, was salicyluret of ammonium, which, by excess of ammonia, was converted into salicylimide.

The salts of the hyduret of salicyle or hydrosalicylic acid, are constituted, for the most part, according to the formula $Sa\ M$. The potassium salt $Sa\ K$, when exposed to the air in a moist state, becomes first green, then black. When the change is complete, water dissolves acetate of potash, and leaves a black matter, *melanic acid*, $C_{10}\,H_4\,O_5$: 1 eq. of salicyluret of potassium, 2 eqs. water, and 3 eqs. oxygen, contain the elements of 1 eq. acetate of potash, and 1 eq. melanic acid, $C_{14}\,H_5\,O_4, K + 2\ HO + O_3 = C_4\,H_3\,O_4, K + C_{10}\,H_4\,O_5$. Melanic acid combines with bases.

Ettling and Stenhouse have shown that when the salicyluret of copper, $Cu\ Sa = C_{14}\,H_5\,O_4 + Cu$, and the benzoate of copper, $Cu\ O, C_{14}\,H_5\,O_3$, which is isomeric with it, are distilled, several new products are formed. Among these are salicylic acid and two crystalline neutral compounds.

Parasalicyle is a product of the action of heat on salicyluret (salicylite) of copper. Its formula is $C_{14} H_5 O_3$, and it has the composition of anhydrous benzoic acid, or of salicylous acid, (hyduret of salicyle viewed as an oxygen acid), as it exists in its salts. The copper salt from which it is formed may be represented either as $C_{14} H_5 O_4 + Cu$, or as $Cu\,O, C_{14} H_5 O_3$. Parasalicyle is fusible and volatile, and only attacked by strong acids.

When benzoate of copper is distilled, there is formed, besides salicylic acid, a neutral volatile crystalline compound, which contains 1 eq. oxygen less than parasalicyle, and the formula of which is consequently $C_{14} H_5 O_2$. It is therefore isomeric with benzile, and has the composition of the radical benzoyle. Indeed, as it yields benzoic acid when acted on by potash, while benzile yields benzilic acid, it may very probably be that radical. It has not, however, been named by Ettling, who discovered it.

2. Salicylic Acid. $(C_{14} H_5 O_4)\,O, H\,O = SaO, H\,O = Sa\,O_2\,H$.

Formed when hyduret of salicyle is heated with hydrate of potash till the mass loses its brown colour. Hydrogen is given off, and salicylate of potash is formed. Hydrochloric acid, added to the solution of this salt, causes the deposition of crystals of salicylic acid.

The same acid is formed when coumarine, the stearoptene or camphor of the tonka bean, is acted on by caustic potash. Moreover the essential oil of winter-green, or *Gaultheria procumbens*, appears, by the researches of Cahours and Gerhard, to be the salicylate of oxide of methyle. The acid, therefore, is most readily obtained, by gently heating this oil with a slight excess of potash, and afterwards adding an acid, when the salicylic acid, being very sparingly soluble, is deposited. It is easily purified by recrystallisation, and sometimes forms crystals one or two inches in length.

Salicylic acid crystallises in tufts of slender prisms, very like benzoic acid. It may be sublimed without decomposition. The formation of this acid from hyduret of salicyle is very simple: $C_{14} H_5 O_4, H + K\,O, H\,O = C_{14} H_5 O_5, K\,O + H_2$. When the salicylate of potash is decomposed by an acid, the salicylic acid takes up 1 eq. of basic water, and separates as $C_{14} H_5 O_5, H\,O$, or $C_{14} H_5 O_6, H$. The decompositions of this acid are very interesting, connecting it with several other series of organic compounds.

When it is acted on by nitric acid, it is first converted into indigotic acid, or anilic acid, $C_{14} H_4 N O_9, H\,O$, along with other products; and by the continued action of nitric acid, there is finally produced the remarkable bitter acid, called carbazotic, or nitropicric acid, $C_{12} H_3 N_3 O_{13}, HO$. Both these acids are formed from indigo by the action of nitric acid.

When salicylic acid is distilled with caustic baryta, it yields carbonate of baryta, and a heavy oily liquid, which is the acid known as carbolic acid (Runge), and hydrate of phenyle (Laurent), the formula of which is $C_{12} H_6 O_2 = C_{12} H_5, O, H O$. The production of carbolic acid from salicylic acid is easily understood: it is, in fact, analogous to that of benzine from benzoic acid. $C_{14} H_5 O_5, H O + 2 Ba O = 2 (Ba O, C O_2) + C_{12} H_6 O_2$. As the action with baryta is so violent as to destroy a great part of the acid, it'is found better to heat rapidly salicylic acid mixed with powdered glass, when it is resolved into carbolic and carbonic acids.

Now it is very remarkable, that carbolic acid, which is one of the chief ingredients of the oil of coal tar, a product, therefore, of the destructive distillation, is also converted by the action of nitric acid into nitropicric acid. This would indicate that when salicylic acid is acted on by nitric acid, it yields, first, some compound containing the same radical as carbolic and nitropicric acid, and that this is further oxidised into the latter acid. We shall hereafter see that the probable radical of carbolic acid is *phêne*, $C_{12} O_6$, from which, by substitution and oxidation, carbolic and nitropicric acids, and a whole series of compounds, may be formed.

On the whole, from its relation to hyduret of salicyle and to salicine (from which it may also be formed by the action of caustic potash), from its analogy in formation, constitution, and properties to benzoic acid, from its occurrence in nature in the first compound of methyle not artificially produced, and from its ready convertibility into indigotic acid, carbolic acid, and nitropicric acid, salicylic acid is a compound of very great interest.

The salts of salicylic acid have the general formula $C_{14} H_5 O_5, MO$ or $C_{14} H_5 O_6, M$. The salicylate of oxide of methyle, $C_2 H_3 O + C_{14} H_5 O_5$, occurs in the essential oil of *Gaultheria procumbens*, and is much used in perfumery. It gives rise to a number of remarkable products, when subjected to the action of nitric acid, chlorine, bromine, alkalies, &c.; but all these things will be treated of in their proper places.

3. Chlorosalicylic Acid. $C_{14} H_5 \left\{ \begin{matrix} O_4 \\ Cl \end{matrix} \right.$, or $C_{14} H_5 O_4, Cl$.

When dry chlorine is made to act on dry hyduret of salicyle, this compound is formed, along with hydrochloric acid; it crystallises readily, and may be sublimed unchanged. Its formation is entirely analogous to that of chloride of benzoyle, and it might be viewed as chloride of salicyle, $C_{14} H_5 O_4, Cl = Sa\,Cl$. But its properties are those of an acid, and hence we are compelled to consider it as salicylic acid, $C_{14} H_5 O_5$, in which 1 eq. oxygen has been replaced by 1 eq. chlorine, the type remaining unchanged. Hence, after this substitution, it is still an acid, and its true formula is $C_{14} H_5 \left\{ \begin{matrix} O_4 \\ Cl \end{matrix} \right.$ an acid of the type of anhydrous salicylic acid.

With ammonia it forms a new compound, *chlorosalicylimide*. As in the action of ammonia on hyduret of salicyle, so in this case, 2 eqs. ammonia act on 3 of the acid, and 6 of water are separated. The formula of chlorosalicylimide, which is a yellow, insoluble solid, is $C_{42} H_{15} N_2 Cl_3 O_6$; for $3 (C_{14} H_5 Cl O_4) + 2NH_3 = 6 HO + C_{42} H_{15} Cl_3 N_2 O_6$. It is, in fact, salicylimide in which 3 eqs. chlorine have been substituted for 3 eqs. hydrogen.

With bromine and iodine, hyduret of salicyle yields the two analogous compounds, bromosalicylic acid, and iodosalicylic acid; $C_{14} H_5 \left\{ \begin{matrix} O_4 \\ Br \end{matrix} \right.$ and $C_{14} H_5 \left\{ \begin{matrix} O_4 \\ I \end{matrix} \right.$.

4. Nitrosalicylic Acid, $C_{14} H_5 NO_{10} = C_{14} H_4 NO_9, HO$.

Syn. *Anilic acid, Indigotic acid.*—This acid is formed by the action of nitric acid on hyduret of salicyle, or still better, on salicylic acid. It forms yellow prisms, and with bases, yields yellow detonating salts. Ammonia colours it blood-red, and perchloride of iron cherry-red. It would appear, according to the above formula, derived from the analysis of Piria, to be salicylic acid, in which 1 eq. nitrous (hyponitric) acid is substituted for 1 eq. hydrogen. But its characters, and those of its salts, are such as to convince us that it is identical with indigotic, or anilic acid; under which names we shall have again to treat of it.

Appendix to Salicyle.

5. Salicine. $C_{26} H_{18} O_{14} = C_{12} H_{10} O_{10} + C_{14} H_8 O_4$.

This compound occurs in the bark of all such willows as are bitter, such as *Salix helix, S. amygdalina*, &c. It is extracted by boiling with water, decolorising the decoction with litharge, removing the lead dissolved by sulphuric acid and sulphuret of barium, and evaporating to a syrup. The salicine crystallises on standing, in fine scales of a silky lustre, which have a very pure bitter taste, and are highly febrifuge. It is neutral, soluble in water and alcohol, insoluble in ether. Oil of vitriol colours it blood-red. Distilled with bichromate of potash and sulphuric acid, it yields formic and carbonic acids, hyduret of salicyle, and a resinous matter.

6. Saligenine. $C_{14} H_8 O_4$.

The recent researches of Piria have very greatly extended our knowledge of salicine. The formula above given for salicine is deduced from his analyses, and he has shown that by contact with synaptase, salicine is decomposed, being resolved into *sugar*, $C_{12} H_{10} O_{10}$, (which takes up 4 eqs. of water and appears as grape sugar, $C_{12} H_{14} O_{14}$) and a new body, *saligenine*, $C_{14} H_8 O_4$. When the metamorphosis is complete, which, with 200 parts of water, and 3 parts of synaptase for 50 of salicine, and a temperature of 106°, takes place in 24 hours, most of the saligenine separates in crystals, being very sparingly soluble in cold water, and the rest is obtained by agitating the solution with ether, which dissolves the saligenine. The aqueous liquid is now found to contain only grape, sugar, and the residue of the synaptase.

Saligenine melts at 180°, and form on cooling a crystalline mass. It appears to form a combination with potash, but when it is heated with that alkali, hydrogen is disengaged and salicylic acid is formed. Several oxidising agents convert saligenine into hyduret of salicyle, from which it differs only by containing 2 eqs. of hydrogen more. Aqueous solutions of perchloride of iron and of salts of peroxide of iron strike an indigo blue with saligenine; but this colour is not formed when alcoholic or etherial solutions are used. The blue compound has not been separated. When heated to a certain point, or boiled with acids, saligenine is converted into *saliretine*, a body which is also obtained when salicine is boiled with dilute acids, and which is no doubt in this latter case derived from the saligenine contained in the salicine. Saliretine will be described presently.

As it appears certain from the experiments of Piria that salicine is composed of saligenine and sugar, the products of various reactions on salicine will be generally those on a mixture of saligenine and sugar. It will therefore be better to describe in connection the substances produced from saligenine, and those formed from salicine.

By the action of chlorine on salicine, there are formed three compounds analogous to salicine, in which 1, 2, and 3 eqs. of hydrogen are replaced by chlorine.

These are :—

Chlorosalicine . . . . $C_{26}\left.\begin{matrix}H_{17}\\Cl\end{matrix}\right\}O_{14} + 4\text{ aq.}$

Bichlorosalicine . . . $C_{26}\left.\begin{matrix}H_{16}\\Cl_2\end{matrix}\right\}O_{14} + 2\text{ aq.}$

Terchlorosalicine . . . $C_{26}\left.\begin{matrix}H_{15}\\Cl_3\end{matrix}\right\}O_{14} + 2\text{ aq.}$

These compounds are all crystallised, and all of them, like salicine, are decomposed by fermentation in contact with synaptase into sugar and a body derived from saligenine.

Thus we have :—

Chlorosalicine = Sugar + Chlorosaligenine,

$$C_{26}\left.\begin{matrix}H_{17}\\Cl\end{matrix}\right\}O_{14} = C_{12}H_{10}O_{10} + C_{14}\left.\begin{matrix}H_7\\Cl\end{matrix}\right\}O_4;$$

Bichlorosalicine = Sugar + Bichlorosaligenine,

$$C_{26}\left.\begin{matrix}H_{16}\\Cl_2\end{matrix}\right\}O_{14} = C_{12}H_{10}O_{10} + C_{14}\left.\begin{matrix}H_6\\Cl_2\end{matrix}\right\}O_4;$$

and

Terchlorosalicine = Sugar + Terchlorosaligenine,

$$C_{26}\left.\begin{matrix}H_{15}\\Cl_3\end{matrix}\right\}O_{14} = C_{12}H_{10}O_{10} + C_{14}\left.\begin{matrix}H_5\\Cl_3\end{matrix}\right\}O_4.$$

Chlorosaligenine forms very fine crystals, and is singularly like saligenine in its outward characters. It colours oil of vitriol, however, green, whereas saligenine colours it red, as does also salicine. The two other compounds are obtained with much greater difficulty by the action of synaptase or Bichlorosalicine and Terchlorosalicine owing to the very sparing solubility of these compounds. But their existence has been established.

7. Saliretine.

When saligenine is boiled with diluted acid, or heated beyond its melting point, it is changed into a resinous substance, which differs from saligenine only by 2 eqs. water. Its empirical formula is $C_{14}H_6O_2$, and therefore it is isomeric or polymeric with hyduret of benzoyle.

It appears that Chlorosaligenine, Bichlorosaligenine, and Terchlorosaligenine also yield resins when boiled with acids, and these resins are in all probability derived from saliretine, and composed of $C_{14}\left.\begin{matrix}H_5\\Cl\end{matrix}\right\}O_2$, $C_{14}\left.\begin{matrix}H_4\\Cl_2\end{matrix}\right\}O_2$, $C_{14}\left.\begin{matrix}H_3\\Cl_3\end{matrix}\right\}O_2$. If so, they will be named Chlorosaliretine, Bichlorosaliretine, and Terchlorosaliretine.

8. Helicine. $C_{26} H_{16} O_{14} = C_{12} H_{10} O_{10} + C_{14} H_6 O_4$.

This compound is formed when salicine is acted on by diluted nitric acid. When pure it forms small white needles, which contain, in addition to twice the above formula, 3 eq. of water of crystallisation. Helicine contains the elements of sugar and hyduret of salicyle, and is actually resolved into them by synaptase, and in other ways. It is no doubt formed by the oxidation of the saligenine producing hyduret of salicyle, which then unites with the sugar to form helicine.

Helicine, when heated to 347°, is converted into an insoluble resinous mass.

When the oxidation of salicine is carried further, the sugar is destroyed, and yields formic and carbonic acids; but when the oxidation is insufficient to form helicine, there is produced a body, *helicoidine*, the empirical formula of which is $C_{52} H_{34} O_{28} + 3$ eq. $= 2$ eq. sugar, $C_{24} H_{20} O_{20}$; 1 eq. hyduret of salicyle, $C_{14} H_6 O_4$; and 1 eq. saligenine, $C_{14} H_8 O_4$.

By the action of chlorine, helicine yields chlorohelicine $C_{26} \left.\begin{matrix} H_{15} \\ Cl \end{matrix}\right\} O_{14}$, which is formed of sugar and chloride of salicyle, $C_{12} H_{10} O_{10} + C_{14} \left.\begin{matrix} H_5 \\ Cl \end{matrix}\right\} O_4$. With bromine it yields a similar compound.

Rutiline is the name given to the red compound formed by the action of oil of vitriol on salicine. When pure it is of a deep reddish-brown colour: acids change it to a bright red, alkalies to a deep violet.

9. Phloridzine. $C_{42} H_{29} O_{24} = C_{42} H_{23} O_{18} + 6 HO$?

This is a substance, very analogous to salicine, which occurs in the bark of the roots of the apple, pear, plum, &c. It is extracted in the same way as salicine, and resembles it much; forming small scales, soluble in hot water, and in alcohol, very bitter, and powerfully febrifuge. When boiled with dilute sulphuric acid, it yields a resinous compound, *phloretine*, analogous to saliretine, along with grape sugar. Phloretine is $C_{30} H_{15} O_{10} = C_{30} N_{14} O_9, HO$? and $C_{30} H_{15} O_{10} + C_{12} H_{14} O_{14} = C_{42} H_{29} O_{24}$. According to Stas, however, phloretine is $C_6 H_3 O_2$, or double or quadruple of this. The compound of phloretine with oxide of lead he found to be $C_{12} H_5 O_3, 2 PbO$; which would indicate, for hydrated phloretine, $C_{12} H_5 O_3, 2 HO = C_{12} H_6 O_4, HO = C_{12} H_7 O_5$?

By the action of nitric acid on phloridzine, there is formed a puce-coloured acid, nitrophloretic acid, which, according to Piria, is $C_{30} H_{12} NO_{15}$; according to Stas, $C_{24} H_{10} NO_{12}$.

Phloridzéine. $C_{42} H_{29} N_2 O_{26}$? When moist phloridzine is exposed to air and ammonia, it is transformed into a deep red compound, which dissolves in ammonia, and may be precipitated by acids. It is equal to phloridzine, *plus* 8 eqs. oxygen, and 2 eqs. ammonia. When dissolved in ammonia, and dried in vacuo, it leaves a purple mass, with coppery lustre, which communicates to water a splendid blue colour. This is a compound of phloridzéine and 1 eq. ammonia. The formation of this blue pigment is a very good example of that kind of eremacausis with the aid of ammonia, by which indigo, litmus, orchil, &c. are produced from colourless bodies.

When salicine was supposed to be $C_{42} H_{29} O_{22}$, phloridzine appeared to differ from it by only 2 eqs. oxygen; but as that formula for salicine, according to Piria, is erroneous, it is most probable that the formula of phloridzine will require to be changed. It is therefore marked as doubtful, along with its derivatives.

XV. CINNAMYLE. $C_{18} H_8 O_2 = Ci$.

The radical of essence of cinnamon, but unknown in a separate form.

1. Hyduret of Cinnamyle. $Ci\,H = C_{18} H_9 O_2 = C_{18} H_8 O_2, H$.

This is the purified essence, or oil of cinnamon. The oil of commerce contains, besides, cinnamic acid and two resins, all of which have been produced from the original oil, $C_{20} H_{11} O_2$ by the additions to 3 eqs. of it, of 8 eqs. oxygen. $3 (C_{20} H_{11} O_2) + O_8 = C_{18} H_8 O_4$ (cinnamic acid) $+ C_{12} H_5 O$ (a resin); $+ C_{30} H_{15} O_4$ (another resin), $+ 5\,HO$. With less oxygen, hyduret of cinnamyle, $C_{18} H_8 O_2$, is formed, along with the resins, so that the oil of commerce contains, besides the original oil, all the compounds above mentioned.

The hyduret of cinnamyle, $Ci\,H$, is a fragrant oil. It forms, with nitric acid, a crystalline compound, $Ci\,H + NO_5$, which, when mixed with water is resolved into its constituents, hyduret of cinnamyle and nitric acid. When the hyduret is exposed to the air, it absorbs oxygen, producing cinnamic acid, $Ci\,O, HO = C_{18} H_8 O_3, HO$.

The fresh oil of cinnamon is, as has been stated, $C_{20} H_{11} O_2$. With 6 eqs. oxygen from the air, it yields hyduret of cinnamyle and the two resins: with 2 eqs. more, the hyduret passes into cinnamic acid. With oil of vitriol, 3 eqs. of the fresh oil $= C_{60} H_{33} O_6$, lose 3 eqs. water, and form two resins, one $= C_{30} H_{15} O$; the other $= C_{30} H_{15} O_2$. With hydrochloric acid, it yields an oil and two resins; one, $C_{20} H_8 O$; the other $C_{14} H_6 O$.

2. Cinnamic Acid. $C_{18} H_7 O_3 + H O = Ci O, H O$.

Formed by exposing oil of cinnamon to the air. It is most easily obtained by dissolving the oil of balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving in hot water, and adding to the solution of cinnamate of potash an excess of hydrochloric acid. It crystallises very readily, and may be sublimed. By the action of nitric acid, cinnamic acid is converted into hyduret of benzoyle, and into an acid very similar to benzoic acid, if not identical with it. When cinnamic acid is added to cold nitric acid, it forms an acid, $C_{18} H_7 NO_8 = C_{18} H_8 O_4 - H + NO_4$; that is, cinnamic acid, in which 1 eq. of nitrous acid is substituted for 1 of hydrogen; $C_{18} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right. O_3, HO$. This is *nitrocinnamic acid.* Its salts detonate when heated. With oxide of ethyle, it forms a crystallisable ether, $Ae\ O, C_{18} H_6 NO_7$. When oil of cinnamon is mixed with fuming sulphuric acid, there is formed, according to Herzog, a new acid, sulphocinnamic acid, the formula of which is $C_{18} H_6 O_2, 2SO_3 + 2 HO = C_{18} H_8 O_{10} S_2$. It is bibasic, and almost all its salts are soluble.

When oil of cinnamon is acted on by nitric acid with the aid of heat, it yields benzoic and nitrobenzoic acids. By the action of chlorine, oil of cinnamon is converted into several new products, one of which is *chlorocinnose*, $C_{18} \left\{ \begin{matrix} H_4 \\ Cl_4 \end{matrix} \right. O_2$. It is hyduret of cinnamyle in which 4 eqs. of chlorine are substituted for 4 eq. of hydrogen.

Balsam of Peru contains compounds connected with cinnamyle. The principal is an oil, *cinnameine*, which, when boiled with alkalies, yields cinnamic acid and a neutral oily body, *peruvine*, $C_{18} H_{12} O_2$. Cinnameine, heated with dry potash, yields hydrogen gas and pure cinnamate of potash. When exposed to cold, cinnameine deposits crystals, which have the same composition as hyduret of cinnamyle, and are therefore an isomeric modification, analogous to benzoine.

According to Richter, balsam of Peru contains two distinct oils, *myroxiline*, insoluble in alcohol, and *myriospermine*, soluble in alcohol. With an alcoholic solution of potash, myriospermine yields an acid resembling cinnamic acid, but different from it, *myriospermic acid.*

Balsam of Tolu.

Tolene ; Benzoene.

According to Deville, Balsam of Tolu contains benzoic acid, and a body isomeric with hyduret of benzoyle ; also, cinnameine, and a liquid carbo-hydrogen, *tolene*, the formula of which is $C_{24} H_{18}$; besides several resins, and another liquid carbo-hydrogen, analogous to benzole, the name given to which is *benzoene*, and its formula $C_{14} H_8$. It boils at 226°, and its Sp. G. is 0·87 at 65° F. When acted on by nitric acid, benzoene yields two new compounds, in which the hydrogen is partly replaced by nitrous acid. These are, 1*st*, *protonitrobenzoene*, $C_{14} H_7 NO_4$, which is liquid ; and, 2*nd*, *binitrobenzoene*, $C_{14} H_6 N_2 O_8$, which is a crystalline solid. By the action of chlorine on benzoene, Deville has also obtained a series of compounds in which the hydrogen is replaced by chlorine ; these compounds, however, chiefly occur in combination with hydrochloric acid. Benzoene dissolves in forming sulphuric acid, and forms a crystalline mass of sulphobenzoenic acid, the composition of which, according to Deville, is $C_{14} H_7 S_2 O_5$; that is, 1 eq. of hydrogen seems to be replaced by 1 eq. hyposulphuric acid. Perhaps a better name for this acid would be hyposulphobenzoenic acid. It is analogous to the sulphonaphthalic or hyposulphonaphthalic acid.

XVI. Guaiacyle. $C_{14} H_7 O_4$?

Hyduret of Guaiacyle. $C_{14} H_8 O_4 = C_{14} H_7 O_4 + H$?

When the resin, or gum resin, called Guaiacum, is distilled, there is obtained, among other products, a colourless oily liquid, which has acid properties. According to Deville, it is analogous to the hyduret of salicyle, which is also an acid, and is sometimes called salicylous acid. Indeed, Sobrero, who first obtained the acid from Guaiacum, called it pyroguaiacic acid. If viewed as a hydrogen acid, it will be the hyduret of guaiacyle, $C_{14} H_7 O_4 + H$, and this agrees with the formula deduced from analysis $C_{14} H_8 O_4$, which is that of saligenine. The acid corresponding to salicylic acid has not been formed, but will probably hereafter be obtained. Its formula will be $C_{14} H_8 O_6 = C_{14} H_7 O_5, HO$. But Thierry has obtained another acid, which he calls guaiacic acid, the formula of which is $C_{12} H_8 O_6 = C_{12} H_7 O_5, HO$. Deville has also described another oil, which is neutral, and seems to be derived from this last acid, as benzole from benzoic acid. Its formula is

$C_{10} H_8 O_2$; and it is derived from the acid $C_{12} H_8 O_6$ by the separation of 2 eqs. carbonic acid; for $C_{12} H_8 O_6 - 2 CO_2 = C_{10} H_8 O_2$. This neutral oil has been called guaiacéne.

In the preceding pages we have considered a large number of compound radicals, constituting chiefly the group of radicals analogous in their relations to chlorine; namely, cyanogen; ferrocyanogen and its numerous congeners; sulphocyanogen; and mellone. We have only described one radical, *amide*, which has a tendency to produce basic compounds, such as *ammonia*, *ammonium*, and the *platinised bases;* and one, *carbonic oxide* or *oxalyle*, the chief tendency of which is to form acid compounds, such as *oxalic*, *carbonic*, *rhodizonic*, *croconic*, and *mellitic* acids. Finally, we have studied three; namely, *benzoyle*, *salicyle* and *cinnamyle*, whose characteristic is to form essences or fragrant volatile compounds, with hydrogen, acids with oxygen, and peculiar compounds with chlorine, iodine, &c. This last group would appear to have a strong tendency to form acid compounds: for not only is an acid formed by the union of salicyle and oxygen, but the hyduret of salicyle is a decided acid, and may be represented as salicylous acid, $C_{14} H_5 O_3$, HO, isomeric with benzoic acid, instead of hyduret of salicyle, $C_{14} H_5 O_4$, H. Further, the chloride, bromide, and iodide of salicyle, although they contain salicyle, *plus* those elements, are all strong acids, and appear to be in fact *anhydrous salicylic acid* with 1 eq. of chlorine, &c. substituted for 1 eq. of *oxygen*. It is evident that this group of radicals, so well characterised by their hydrogen compounds, does not correspond exactly to any simple radical, but has characters common to different groups of elementary radicals, being, however, analogous in more points to carbon, sulphur, and phosphorus than to any other elements. In studying the decomposition of the compounds of salicyle, we have met with the very remarkable fact of the production from that radical of a series of compounds: namely, anilic acid, nitropicric acid, carbolic acid, &c., probably derivatives of a totally different radical, phenyle; which radical is also met with in numerous other decompositions, and especially in the decomposition of indigo by nitric acid, by alkalies, and by heat, and in the destructive distillation of coal. This is an important consideration, as every day's experience tends to identify with each other the products of decomposition of different and apparently quite unconnected organic compounds, even in cases where these products have been described as different. Another very important fact which has come under our notice is the occurrence of salicylate of oxide of methyle as the chief ingredient in the oil of Gaultheria. Not only is the occurrence of salicylic acid interesting, since this acid was only known before as an artificial product, but the existence, in this oil, of oxide of methyle, hitherto only known as a product of destructive distillation, goes far to confirm the theory which admits this radical, methyle, and others similar to it. All the properties of the oil of Gaultheria entirely agree with the doctrine of its containing two radicals, methyle and salicyle, the former oxidised, as a base; the latter, also oxidised, as an acid. It is remarkable, however, that even this compound plays the part of an acid, and forms crystalline salts with the alkalies into which it enters unchanged. This is so well marked a character that the oil has been called gaultheric acid, and the salts gaultherates.

We now proceed to consider that group of radicals to which methyle belongs, and which are analogous, in their relations, to metals, more than to any other class of elements; forming, like metals, bases with oxygen. This group contains Ethyle, Methyle, Amyle, Glyceryle, Cetyle, Allyle, and Cacodyle; besides several radicals, derived from the decomposition of these; as, Acetyle from Ethyle, Formyle from Methyle, and Acryle from Glyceryle. These latter, however, belong to that group which are analogous to the combustible metalloids, and form acids with oxygen, instead of bases, like the radicals from which they are derived, and in connection with which they shall be described.

XVII. ETHYLE. $C_4 H_5 = Ae$.

Unknown hitherto in a separate form; but very well known as anhydrous oxide, or ether, and hydrated oxide, or alcohol. These compounds have not yet been found as natural products of vegetable life, although it is probable that the fragrance of certain fruits, such as pine-apples, melons, apples, is derived from compounds of ethyle. The compounds of ethyle, especially alcohol, are, however, very abundantly produced by the fermentation of saccharine vegetable juices, such as that of the grape. The alcoholic or vinous fermentation of sugar is a metamorphosis, induced in the sugar by contact with yeast or ferment, which is gluten or fibrine in a state of decomposition. In this metamorphosis, the particles of the ferment only act in communicating mechanical motion to those of the sugar; they do not join the elements of the sugar in producing new compounds, but are decomposed separately; while the elements of the sugar, *plus* a small proportion of the elements of water, form two compounds, alcohol and carbonic acid. $C_{12} H_{11} O_{11} + HO = 2 (C_4 H_5, O + HO) + 4 C O_2$. Grape sugar $C_{12} H_{14} O_{14}$, loses 2 eqs. of water during fermentation, yielding otherwise exactly the same results as cane sugar. Sugar of milk, $C_{12}H_{12}O_{12}$, is converted by fermentation into alcohol and carbonic acid, without losing or gaining weight. $C_{12}H_{12}O_{12} = 2(C_4H_6O_2) + 4CO_2$.

1. Oxide of Ethyle. $AeO = C_4H_5, O$.

Syn. *Ether. Sulphuric Ether.*—This compound is obtained from alcohol, its hydrate, by heating it gently along with sulphuric or phosphoric acid, which removes the water, or at all events causes the separation of the ether from the water. The best process is as follows: 5 parts of alcohol, of at least 90 per cent., are mixed with 9 of sulphuric acid, and the mixture introduced into a retort, where it is rapidly heated to the boiling-point, and kept at that point, while by means of a bent tube passing through the cork which stops the tubulure of the retort, and furnished with a stop-cock, fresh alcohol is allowed to enter the retort so as to keep the liquid constantly at the original level, flowing in exactly as fast as the ether, &c., distils over. The products are condensed in a powerful refrigeratory, such as Liebig's, figured at p. 299; they consist chiefly of ether, with water in such proportion as would convert the ether into alcohol; and a very little alcohol, sometimes none at all. The operation may be advantageously continued until 31 parts of alcohol, at 90 per cent., have flowed into the retort, and of course an equal volume of ether and water has distilled over.

This process, as to its final result, may be thus expressed. $AeO, HO + 2(HO, SO_3) = 2(HO, SO_3) + HO + AeO$. That is, the action of heat and of oil of vitriol has caused the separation of the ether and the water, which, together, constitute alcohol. And it is to this view of the change, which he considers one of decomposition by contact, that Berzelius applies his theory of a catalytic force. But in reality, the process consists of two stages: the first is the formation of bisulphate of oxide of ethyle (sulphovinic acid) $AeO, HO, 2SO_3$; and the second is the decomposition of this by heat into AeO and $HO, 2SO_3$. The bisulphate is formed when a mixture of 2 eq. oil of vitrol, 1 eq. alcohol, and from 1 to 3 eq. of water, is heated to about 285°; and at almost precisely the same temperature, the bisulphate is decomposed, especially if the liquid be kept in steady ebullition. Now, the bisulphate contains anhydrous sulphuric acid, ether, and water, $2SO_3 + AeO + HO$; and when decomposed the sulphuric acid seizes the water, thus preventing the ether from uniting with it to reproduce alcohol. The ether, therefore, distils over: but as, when the bisulphate was formed, ether, AeO, displaced water, HO, from half the oil of vitriol, so now, when the bisulphate is decomposed, and while its water is retained by the 2 eq. of anhydrous acid, the vapours of ether traverse a liquid containing oil of vitriol diluted, both with the water displaced from the other part of it by the ether, and with the water of the alcohol (which at 90 per cent. amounts to 2 eq. for 1 of ether, one combined with the ether to form the alcohol, the other serving to dilute it.) Now, a sulphuric acid, thus far diluted, and heated to a temperature even short of 285°, gives off water, and therefore the vapour of ether in passing through this acid, becomes saturated with the vapour of water, without combining with it, and thus ether and water distil over together. At the surface of the boiling, or effervescing liquid, however, the ether produced by the decomposition of the bisulphate is brought into contact with water in the nascent state, also derived from that decomposition, and in this manner, according to Liebig, a little alcohol is reproduced, and distils over with the ether, the ether being produced in the body of the liquid, the alcohol only at the surface. It is certain that a little alcohol generally accompanies the ether, even in the most successful operation; but it is not easy to see how, according to the above explanation, the sulphuric acid which, in the body of the liquid, is able to prevent the ether from combining with water, should fail to do so at the surface. The ether and water, it would appear, are equally in the nascent state in both situations. While, therefore, we admit Liebig's very beautiful explanation of the facts connected with the production of ether, we cannot feel the same certainty in regard to his explanation of the simultaneous occurrence of alcohol. It will now be seen how little necessity there is for resorting to the mysterious agency of catalysis; for the change is not one due to contact alone, but, on the contrary, one depending on strong affinities very nicely balanced, and influenced to a very great extent by the degree of heat employed. The idea that the contact of oil of vitriol caused the ether and water of alcohol to separate, arose from the circumstance that the formation of the bisulphate of ethyle takes place at a temperature quite close to that at which it is decomposed, and that the formation of the bisulphate in this process had been overlooked.

The crude ether is mixed with an alcoholic solution of potash, so as to render it alkaline, and distilled in the vapour-bath, as long as the Sp. G. of the product does not exceed 0·725 at 80°. The ether is then digested for a few days with chloride of calcium, or quicklime, and rectified once more with one of these substances. When pure, oxide of ethyle is a colourless, very mobile, highly refracting liquid, of Sp. G. 0·725° at 60°. It is very volatile, boiling at 76°, and producing intense cold by its evaporation. It has a pungent, cooling, aromatic taste; and a penetrating, agreeable odour. It is very combustible, and its vapour is apt to form dangerous explosive mixtures with air. When oxidised slowly, it yields aldehyde, aldehydic acid, acetic and formic acids.

Ether is used in medicine as a diffusible stimulant, and in chemistry, as a solvent, especially of organic matters, such as fats, fat oils, essential oils, resins, some acids, and some bases. Its vapour, when mixed with air and inhaled, produces a species of coma, or at least, in most cases, insensibility to pain; and this method is now resorted to to facilitate the performance of severe surgical operations. Great care must be taken to avoid the approach of a light to the mouth of the patient inhaling it, which might cause explosion of the gaseous mixture, or inflammation of the ether, and thus inflict a fatal injury. Care must also be taken to have air enough mixed with the vapour of ether, which, if inhaled alone, would cause asphyxia.

In its relations to other bodies it exhibits the characters of a base, neutralising acids, and forming compounds which are subject to the laws of double decomposition, like salts of inorganic bases. These salts of oxide of ethyle are, commonly, ethereal liquids; many of them crystallising at low temperatures, and a good many being solid and crystalline at ordinary temperatures. They are often called ethers, with the name of the acid; as, acetic ether, benzoic ether, &c. Those ethers which contain organic acids are for the most part fragrant, and it is probable that many fruits owe their fragrance to the presence of the ethers of organic acids. The melon and pine apple, as well as the apple, have exactly the odour of some such ethers. The formula for the salts of oxide of ethyle corresponds to that for the salts of potash, &c. Thus, as $\text{K O}, \overline{\text{A}}$ represents acetate, and $\text{K O}, \overline{\text{Bz}}$ benzoate of potash, so $\text{Ae O}, \overline{\text{A}}$ or $\text{Ae O}, \text{Ac O}_3$, and $\text{Ae O}, \overline{\text{Bz}}$ or $\text{Ae O}, \text{Bz O}$ represent the acetate and benzoate of oxide of ethyle.

The analogy between ether and metallic protoxides is further shown in the action of both on hydrochloric acid and its congeners; for while K O, with H Cl yields H O and K Cl; so $\text{Ae O} + \text{H Cl} = \text{H O} + \text{Ae Cl}$: that is, ether, with hydrochloric acid, yields water and chloride of ethyle. The same is true of the bromide, iodide, &c., and by proper means both the cyanide of ethyle, Ae Cy, and the sulphuret of ethyle, Ac S, may be obtained. In short, we cannot better connect and classify the numerous facts now known in regard to ether, than by adopting the view which considers it as the basic oxide of ethyle, a compound radical, very analogous to a metal.

2. *Hydrate of oxide of ethyle.* $AeO, HO = C_4H_5O, HO$. SYN. *Alcohol.* This compound is formed when ether and water meet in the nascent state, as we shall see occurs when some of the acid salts of ethyle are heated, or otherwise decomposed. But, practically, it is produced entirely from sugar by fermentation. The juice of the grape, or any other saccharine juice, or an infusion of malt, when exposed to the air for a short time, and then to a temperature of from 40° to 85°, soon enters into fermentation, and a large quantity of carbonic acid is given off, while the sugar totally disappears, and alcohol is found in its place. A pure solution of sugar in water does not ferment, but on the addition of yeast it does so. The juice of the grape and the infusion of malt both contain, besides sugar, some body which plays the part of yeast, or ferment. This is, in the grape juice, fibrine, and in the malt, gluten, both of which readily enter into putrefaction when exposed to air and moisture, and being in this state, their particles in motion, this motion is communicated to the particles of sugar, and the existing equilibrium of affinities being thereby disturbed, new compounds are formed, in this case alcohol and carbonic acid. The subject of fermentation will be afterwards fully discussed: in the mean time, it is to be observed that any similar substance, in a state of putrefaction, will induce the fermentation of sugar; as, for example, putrefying flesh, blood, milk, cheese, white of egg, urine, &c. &c., and that none of these ferments contribute to the production of the alcohol, or carbonic acid, but yield ammonia and other products. Crystallised cane sugar, $C_{12}H_{11}O_{11}$, requires the elements of 1 eq. of water to yield 2 eq. alcohol $C_8H_{12}O_4$ and 4 eq. carbonic acid $4\,CO_2 = C_4O_8$; and grape sugar, $C_{12}H_{14}O_{14}$, produces, besides the alcohol and carbonic acid, 2 eq. of water. Thus we have $C_{12}H_{11}O_{11} + HO = 2\,(C_4H_6O_2) + 4\,CO_2$; and $C_{12}H_{14}O_{14} = 2\,(C_4H_6O_2) + 4\,CO_2 + 2\,HO$.

From the fermented liquid, which, in the case of the grape juice, is wine, in that of malt, beer, ale, or wort, the alcohol is separated by distillation, and being more volatile than water, it predominates in the first portions distilled. These constitute, when from wine, brandy; when from a fermented infusion of malt, whiskey; and when from fermented solution of molasses, rum. In these forms it still contains 30, 40, or more per cent. of water, and a little volatile odoriferous oil. It is again rectified, and the first portions distilled are colourless, and go by the name of spirits of wine. After another rectification they are called rectified spirits of wine. They now contain only alcohol, with from 10 to 20 per cent. of water, which is removed by digesting the spirit with quicklime, and distilling: or by rectifying over dried carbonate of potash, or chloride of calcium.

Pure or absolute alcohol is a colourless mobile fluid of Sp. G. 0·795 at 60°, and boiling at 173°. It has a burning taste, and a pleasant fruity smell. Rectified spirit of wine, that of 90 per cent., is very similar to it, having the Sp. G. 0·825 to 0·836: ordinary spirit of wine, at 70 per cent., has the Sp. G. 0·880. Pure alcohol has never been frozen. It is very combustible, and produces, in burning, a very intense heat. Hence spirit of wine is much used for lamps for chemical purposes. Alcohol has a strong attraction for water, and on this account acts as an antiseptic, preserving animal and vegetable substances from putrefaction. The strength of alcohol is ascertained by its specific gravity; and all chemical works contain tables of the relation between the density of the spirit and the per centage.

Alcohol is a powerful diffusible stimulant, and has intoxicating properties. It is much used as a solvent, for many, indeed most vegetable acids and bases, for volatile oils, for resins, and for many salts, even inorganic. Most deliquescent salts are soluble in alcohol, as are the caustic alkalies and iodine. Acids act on alcohol, producing the compound ethers. Solutions made with proof spirit (a mixture of equal volumes of rectified spirit of wine and of water, Sp. G. 0·960), are called tinctures.

3. *Chloride of ethyle*, $Ae\,Cl = C_4\,H_5, Cl$, is prepared by saturating alcohol with hydrochloric acid gas, and distilling the mixture in the vapour bath, collecting the product in a well cooled receiver. It is formed as follows: $Ae\,O, H\,O + H\,Cl = Ae\,Cl + 2\,H\,O$. It is dried by digestion with chloride of calcium. It is a colourless liquid, Sp. G. 0·874, boiling at 52°, of an aromatic odour, slightly alliaceous. When exposed to the combined action of chlorine and the sun's rays, it yields by substitution a whole series of chlorinised ethers, of which series one extremity is ether $(C_4\,H_5)\,O$; and the other, perchloride of carbon $(C_4\,Cl_5)\,Cl = 2\,C_2\,Cl_3$. With an alcoholic solution of protosulphuret of potassium $K\,S$, it gives chloride of potassium and sulphuret of ethyle. $Ae\,Cl + K\,S = Ae\,S + K\,Cl$. With hydrosulphuret of sulphuret of potassium, it yields *mercaptan*, which is alcohol, in which all the oxygen has been replaced by sulphur. $Ae\,Cl + K\,S, H\,S = K\,Cl + Ae\,S, H\,S$; the latter, mercaptan, being analogous to $Ae\,O, H\,O$.

4. *Bromide of ethyle*, formed by distilling bromine with alcohol and phosphorus. These are first formed, when the materials

are mixed, phosphorous and hydrobromic acids, and the latter when heated with the alcohol, decomposes it yielding $\mathrm{Ae\,Br}$, which resembles the chloride.

5. *Iodide of ethyle*, $\mathrm{Ae\,I}$, formed by a similar process, is analogous to the two preceding compounds.

6. *Sulphuret of ethyle*, $\mathrm{Ae\,S}$, is prepared, as above stated, from the chloride by sulphuret of potassium. It is a colourless liquid, boiling at 167°, of a strong offensive alliaceous smell.

7. *Hydrosulphuret of sulphuret of ethyle* or *mercaptan*, $\mathrm{Ae\,S, H\,S = C_4\,H_6\,S_2}$ or $\mathrm{C_4\,H_5, S + H\,S}$. This very remarkable compound is formed when a solution of the double sulphate of lime and oxide of ethyle (sulphovinate of lime) of Sp. G. 1·28, is distilled with its own bulk of a solution of potash of the same density, previously saturated with sulphuretted hydrogen, and converted into $\mathrm{KS, HS}$. The volatile product, after digesting it with a little oxide of mercury and chloride of calcium, to remove sulphuretted hydrogen and water, is mercaptan. Its formation is thus explained: $\mathrm{(Ca\,O, SO_3 + Ae\,O, SO_3) + KS, HS = Ca\,O, SO_3 + K\,O, SO_3 + Ae\,S, HS}$. Pure mercaptan is a colourless liquid, very mobile, boiling at 97°, of Sp. G. 0·842. It has a most penetrating and offensive odour of onions, as it were concentrated, which adheres obstinately to the hair or clothes, so that it is most unpleasant to experiment upon. As above mentioned, it is formed from alcohol by substitution of sulphur for oxygen; and as alcohol is the hydrate of oxide of ethyle, $\mathrm{Ae\,O, H\,O}$, mercaptan is the hydrosulphuret of the sulphuret of ethyle, $\mathrm{Ae\,S, H\,S}$. The sulphuret of ethyle, $\mathrm{Ae\,S}$, corresponds to the oxide, ether, $\mathrm{Ae\,O}$.

Mercaptan acts strongly on some metallic oxides, especially those of the noble metals, such as mercury, gold, platinum, &c. The metal takes the place of the hydrogen of the sulphuretted hydrogen in mercaptan; thus $\mathrm{M\,O + (Ae\,S, H\,S) = H\,O + (Ae\,S, M\,S)}$. The red oxide of mercury is acted on by mercaptan, and converted into a white crystalline compound, called the mercaptide of mercury; oxide of gold forms a gelatinous white mercaptide; and oxide of lead yields lemon yellow crystals of mercaptide of lead, $\mathrm{Ae\,S, Pb\,S}$.

Mercaptan may also be viewed as $\mathrm{H + Ae\,S_2}$, in which case the above metallic compounds will have the general formula $\mathrm{M + Ae\,S_2}$. Here the supposed radical, the *mercaptum* of Zeise, is bisulphuret of ethyle; so that on either view mercaptan is connected with ethyle.

Zeise has described, under the name of thialic oil or ether, another very fetid compound, which seems to be $\mathrm{Ae\,S_3}$, or persulphuret of ethyle.

Seleniuret and cyanide of ethyle are both volatile alliaceous offensive liquids, formed when sulphate of ethyle and potash is distilled with seleniuret or cyanide of potassium. Sulphocyanide of potassium, alcohol and sulphuric acid, when dissolved together, yield a most offensive volatile liquid, supposed to be, or at all events to contain, sulphocyanide of ethyle. It will be observed that all these compounds of sulphur with ethyle and similar bodies are characterised by odours resembling that of garlic, but so intense and penetrating as to be insupportable. This character is observed in all volatile organic compounds of sulphur, whether artificial, as the above, or natural, as oils of garlic, assafetida, horseradish, &c.

7. Salts of Oxide of Ethyle.

Oxide of ethyle forms both neutral and acid salts. The neutral salts are not at ordinary temperatures decomposed by other salts, like inorganic saline compounds. Thus an alcoholic solution of chloride of calcium does not cause any precipitate in an alcohol solution of oxalate of oxide of ethyle or oxalic ether. But they are easily decomposed by contact with hydrated alkalies, the acid uniting with the alkali, while the oxide of ethyle separates as hydrate, that is, as alcohol. Thus oxalic ether $C_2 O_3, Ae\,O$, with hydrate of potash, $K\,O, H\,O$, yields oxalate of potash $K\,O, C_2 O_3$ and hydrate of oxide of ethyle, $Ae\,O, H\,O$.

Oxide of ethyle has a very great tendency to form double salts, in which there are 2 eq. of the acid, 1 eq. of a base, and 1 eq. oxide of ethyle. In these salts, the acid, as in the neutral salts, cannot be detected by the usual tests; and indeed they may be viewed as simple salts, containing a compound acid, of which oxide of ethyle is a constituent, united to the inorganic base. Thus the double sulphate of ethyle and potash, $K\,O, S\,O_3 + Ae\,O, S\,O_3$, may be viewed as sulphovinate of potash, $K\,O + Ae\,O, 2\,S\,O_3$; and sulphovinic acid is, on this view, when separated, $H\,O + Ae\,O, 2\,S\,O_3$.

The acid salts of ethyle are on one view double salts, as, for example, the double sulphate formed of sulphate of ethyle, $Ae\,O, S\,O_3$, with sulphate of water, $H\,O, S\,O_3$. On the other view, they are compound or coupled acids, and the above example becomes, as mentioned in the last paragraph, sulphovinic acid, $H\,O + (Ae\,O, 2\,S\,O_3)$, the hydrate of a compound of anhydrous sulphuric acid with ether. These acid salts are decomposed, by boiling with water, into alcohol which distils over, and hydrated acids which remain behind. When distilled with the salts of volatile acids, they yield the ethers of those acids: formiate and acetate of ethyle may be thus obtained. When an acid salt of ethyle is heated with acids not volatile, it often happens that the ethers of these acids are obtained: this is the case with the fatty acids and with some others.

8. *Acid sulphate of oxide of ethyle*, $HO, SO_3 + Ae SO_3$, is also called *sulphovinic acid*, $HO + (AeO, 2 SO_3)$. Sulphuric acid forms no neutral compound with oxide of ethyle. The acid salt is formed when the vapour of ether is conducted into oil of vitriol, or when oil of vitriol is mixed with alcohol and heated to a certain point. To obtain it pure, the double sulphate of ethyle and baryta (sulphovinate of baryta) in solution, is decomposed by sulphuric acid, and the filtered liquid is a solution in water of the acid sulphate. It has a very sour taste, and cannot be concentrated by evaporation, whether at the ordinary temperature or with the aid of heat, without being decomposed into alcohol and sulphuric acid. It forms, with most bases, crystallisable double salts, which are all soluble, so that, for example, the addition of baryta causes no precipitate if the acid be pure. As the acid sulphate itself is called sulphovinic acid, so these double salts are called sulphovinates. It is because all these salts are soluble, that the usual tests cannot detect the sulphuric acid they contain. When, however, their solutions are boiled with a little hydrochloric acid, alcohol is given off, and then the sulphuric acid may be detected as usual. All these salts are decomposed by heat, yielding, according to the temperature, double sulphate of ethyle and etherole, alcohol, sulphurous acid, olefiant gas, and a sulphate as residue, mixed with charcoal. When heated with hydrated alkalies, they yield sulphates and alcohol. The *double sulphate of ethyle and potash* crystallises in shining scales, which are the anhydrous salt, $KO, SO_3 + AeO, SO_3$. The *baryta salt* contains 2 eq. of water of crystallisation, and forms beautiful tabular crystals, as do also the *salt of lime*, and the *salt of lead*, both of which likewise contain 2 eq. of water. These three salts are all composed according to the formula, $MO, SO_3 + AeO, SO_3, + 2$ eq.

9. *Acid phosphate of oxide of ethyle*, or phosphovinic acid, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2 HO, \end{matrix} \right.$ is formed in the same way as sulphovinic acid, and obtained pure from the double salt of baryta, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2 BaO \end{matrix} \right.$ $+ 12 HO$. It is a tolerably permanent acid, decomposed only by a high temperature. With bases it forms double salts, in which the 2 eq. water of the acid are replaced by 2 eq. of a

protoxide. The *baryta salt,* the formula of which is given above, crystallises in pearly scales.

OXIDE OF ETHYLE WITH NITRIC ACID.

10. Nitrate of Oxide of Ethyle. $Ae\,O, N\,O_5$.

When 2 fluid ounces of alcohol, and 1 fluid ounce of pure nitric acid, of Sp. G. 1·4 are distilled together, with the addition of 10 or 20 grains of urea, to destroy any nitrous or hyponitrous acid, the distillation proceeds calmly and smoothly, and the distilled liquor contains water, alcohol, and nitrate of ethyle, which partly separates, towards the end of the process. as a heavy oily stratum, and is more completely separated by the addition of water. It is a colourless liquid, of Sp. G. 1·112; which boils at 185°, and is inflammable, burning with a bright white flame. It is quite insoluble in water, but very soluble in alcohol; and it possesses a pleasant smell and a sweet taste. An alcoholic solution of potash converts it into alcohol and pure nitrate of potash.

11. Hyponitrite of Oxide of Ethyle. $Ae\,O, N\,O_3$.

Syn. *Nitrous ether.—Nitric ether.* This is best prepared in a state of purity when a current of hyponitrous acid vapours, derived from starch and nitric acid, is passed through weak alcohol, the product being condensed in Liebig's refrigeratory. The ether is washed with water, and dried by means of chloride of calcium. The whole apparatus must be kept cold, otherwise the action is too violent, and the results very complex. When nitrous ether is made by the usual processes, in which ordinary nitric acid is mixed with alcohol, the product always contains a large proportion of aldehyde, and in fact very little of the true ether. The action in this case is as follows, $2\,(C_4\,H_6\,O_2) + N\,O_5 = C_4\,H_3\,O, H\,O$ (aldehyde), $+\,3\,H\,O + (C_4\,H_5, O + N\,O_3)$. The pure hyponitrous ether, prepared by Liebig's process, given above, is a pale yellow liquid, boiling at 62°, of Sp. G. 0·947. It has a very agreeable odour of rennet-apples. With an alcoholic solution of potash, it yields alcohol, and pure hyponitrite of potash. The *sweet spirit of nitre* or *spiritus ætheris nitrosi* of the pharmacopœia, is a solution of the impure hyponitrous ether in alcohol.

12. Carbonate of Oxide of Ethyle. $Ae\,O, C\,O_2$.

Syn. *Carbonic ether.* When oxalic ether is acted on by potassium, there are formed several products, one of which is this ether. When pure, it is an aromatic liquid, of Sp. G. 0·975, boiling at 260°. An alcoholic solution of potash converts it into alcohol and carbonate of potash. Chlorine acts on it, forming products to be described when we treat of the action of chlorine on ethers generally.

13. *Double carbonate of ethyle and potash*, $KO, CO_2 + AeO, CO_2$, is formed when dry carbonic acid gas is passed through an alcoholic solution of fused potash. A saline mass is obtained, from which, after washing with ether, alcohol dissolves the double salt, leaving carbonate and bicarbonate of potash. The double salt forms pearly scales, which are decomposed by water into alcohol and bicarbonate of potash.

14. *Oxalate of oxide of ethyle.* AeO, C_2O_3.—Syn. Oxalic Ether.—This ether is formed by distilling 4 parts of superoxalate of potash, 5 of oil of vitriol and 4 of alcohol at 90 p. c., mixing the product with 4 times its bulk of water, and washing with water the ether which separates, until all free acid is removed. The ether is then rectified. It is a colourless liquid, of Sp. G. 1·093, boiling at 364°. It has an aromatic smell. If pure, it may be kept under water: but if a trace of alcohol or of oxalic acid be present, it is soon resolved into oxalic acid and alcohol when in contact with water. Fixed alkalies cause the same change. When an excess of ammonia is added to it, oxamide is formed: where the ether is in excess, there is formed a substance in beautiful pearly tables, formerly called oxamethane, but now proved to be oxamate of ethyle. These two reactions are easily explained. In the first case, $AeO, C_2O_3 + NH_3 = (AeO, HO) + (C_2O_2, NH_2)$. In the second, half the ether undergoes the above change, and the other half combines with the oxamide formed. $AeO, C_2O_3 + C_2O_2, NH_2 = AeO, C_4NH_2O_5$. Chlorine acts on oxalic ether, giving rise to products which will be hereafter described along with the results of the action of chlorine on other ethers.

When to an alcoholic solution of oxalic ether there is added enough of an alcoholic solution of potash or soda to decompose the half of the ether, double salts are obtained, of the formula $MO, C_2O_3 + AeO, C_2O_3$. When the alcoholic solution of the double oxalate of ethyle and potash is treated by fluosilicic acid, there is obtained the *acid oxalate of ethyle*, $HO, C_2, O_3 + AeO, C_2O_3$, which is often called *oxalovinic acid.* The salt of potash, $KO, C_2O_3 + (AeO, C_2O_3)$ (*oxalovinate of potash*) forms crystalline scales; soluble in alcohol. The *oxalovinate of baryta* is extremely soluble, and may be used to furnish the other oxalovinates, by acting with it on the soluble sulphates of different bases.

15. *Oxamate of oxide of ethyle,* $C_8NH_7O = AeO, C_4NH_2O_5 = AeO, C_2O_3 + Ad, C_2O_2$, is formed, as above stated, when ammonia is cautiously added to an alcoholic solution of oxalic ether, until a white powder (oxamide) begins to appear. The liquid now yields fine pearly tabular crystals, formerly called oxamethane. It now appears to be oxamate of ethyle, but may also be viewed as oxalate of ethyle, *plus* oxamide. By an excess of ammonia, it is converted into alcohol and oxamide. The action of ammonia on oxalic ether has been explained above.

16. *Sulphocarbonate of ethyle and water.* $AeO, HO, 2CS_2$.—When bisulphuret of carbon is added to a strong alcoholic solution of potash, a salt is obtained, in colourless or yellow needles, which is a double sulphocarbonate of ethyle and potash, $KO, CS_2 + AeO, CS_2$. When this salt is acted on by diluted sulphuric or hydrochloric acid, there is obtained a heavy oily liquid. This is the acid compound in question, $HO, CS_2 + AeO, CS_2$, formerly called xanthic acid, from the yellow colour of its salts. With bases it gives rise to double salts, like that of potash, just mentioned, which were called xanthates. The salt of protoxide (suboxide) of copper is lemon yellow.

17. *Allophanate of oxide of ethyle.* This compound is formed when the vapour of hydrated cyanic acid is brought in contact with a mixture of ether and alcohol. It forms brilliant prisms, which may be purified from cyamelide by being dissolved in boiling alcohol, or in boiling water. Its formula is $C_8N_2H_8O_6 = C_4H_5O_1\ C_4N_2H_3O_5$. It was formerly supposed to consist of 2 eqs. hydrated cyanuric acid, 3 eqs. oxide of ethyle, and 3 eqs. of water; and it is, in fact, resolved by heat into alcohol and cyanuric acid. But Liebig and Wöhler have shown that it is composed of oxide of ethyle and of a new acid, namely, anhydrous allophanic acid, $C_4N_2H_3O_5$. The former view was quite anomalous, since oxide of ethyle unites only with anhydrous acids; and the latter, therefore, brings the compound into the ordinary category of compound ethers.

Allophanic acid is unknown in the hydrated or separate state, the formula of which would be $C_4N_2H_3O_5, HO = C_4N_2H_4O_6$. It forms crystallisable salts with baryta, potash and soda; but when we attempt to isolate it, it is resolved into urea and carbonic acid. $C_4N_2H_4O_6 = C_2N_2H_4O_2 + 2CO_2$. Allophanic acid is produced by the action of 2 eqs. of hydrated cyanic acid on 1 eq. of alcohol. The water of the alcohol, added to the cyanic acid, produces the new acid, which combines with the oxide of ethyle. Thus,

$$2\,\underbrace{C_2NO, HO}_{\text{Hydrated cyanic acid.}} + \underbrace{C_4H_5O, HO}_{\text{Alcohol.}} = \underbrace{C_4H_5O}_{\text{Oxide of ethyle.}} + \underbrace{C_4N_2H_3O_5}_{\text{Allophanic acid.}}$$

18. *Benzoate of oxide of ethyle*, or *benzoic ether*, Ae O, BzO, is best formed by distilling 4 parts of alcohol, 2 of benzoic acid, and 1 of strong hydrochloric acid. The ether distils over with alcohol, from which water separates it. When pure, it is an oily, colourless liquid, of a faint agreeable aromatic odour, and an acrid, spicy taste. Its Sp. G. is 1·054, and it boils at about 410°. Chlorine decomposes it, giving rise to several products, probably by substitution.

19. *Hippurate of oxide of ethyle*, or *hippuric ether*, $C_4H_5, O + C_{18}NH_8O_5$, is formed by passing a current of hydrochloric acid gas through a solution of hippuric acid in alcohol, and heating the mixture for some time near to its boiling point. The addition of water separates a thick, heavy oil, which when purified from alcohol and hydrochloric acid, and placed in vacuo, along with sulphuric acid, forms a solid crystalline mass, composed of silky needles. It is decomposed, like other ethers, by alkalies, and by boiling with water.

20. *Salicylate of oxide of ethyle*, $C_4H_5, O + C_{14}H_5, O_5$, is obtained by distilling 2 parts of alcohol, 1½ of salicylic acid, and 1 of sulphuric acid. When purified from alcohol, acid, and water, it is a colourless oily fluid, having a sweet smell like that of the corresponding compound of methyle, which occurs naturally in the oil of *Gaultheria proeumbens*. It is heavier than water, and boils at 437°. Like the oil of Gaultheria, it plays the part of an acid, forming with bases crystallised soluble salts. When exposed to a high temperature with caustic baryta, it yields carbonic acid, and an oil analogous to that obtained from the methyle compound, probably $C_{18}H_{10}O_2$. When fuming nitric acid is added, drop by drop, to the salicylic ether, it dissolves it with a deep red colour: water now separates an oil, which soon concretes into a solid mass, which when dissolved in hot alcohol, yields, on cooling, yellow silky needles. These are *indigotate or anilate of oxide of ethyle*, $C_4H_5, O + C_{14}NH_4O_9$. By the further action of nitric acid, carbazotic or nitropicric acid is obtained. The indigotic ether dissolves in potash and soda, apparently like the salicylic ether, playing the part of an acid. Indigotic ether does not dissolve in ammonia; left in contact within close vessels, it finally disappears, alcohol is reproduced, and there is formed a new product, *anilamide*, $C_{14}N_2H_6O_8$, which, when pure,

forms brilliant yellow crystals. When boiled with potash, anilamide yields anilate (indigotate) of potash, and gives off ammonia; for $C_{14}N_2H_6O_8 + 2HO = NH_3 + C_{14}H_4NO_9, HO$. Bromine acts on salicylic ether, producing two compounds; monobromuretted salicylic ether, $C_{18}H_9BrO_6 = C_4\left\{\begin{matrix}H_4\\Br\end{matrix}\right.O + C_{14}H_5O_5$: and bibromuretted salicylic ether, $C_{18}H_8Br_2O_6 = C_4\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right.O + C_{14}H_5O_5$. The former crystallises in fine needles, the latter in large pearly scales, which, when melted, form, on cooling, a most beautiful crystallisation, formed of large and perfect cubes, like those of bismuth.

COMPOUNDS OF ETHYLE OF UNCERTAIN CONSTITUTION.

1. *Chloro-carbonic Ether*, $C_6H_5ClO_4 = C_4H_5, O + C_2\left\{\begin{matrix}O_3\\Cl\end{matrix}\right.$? Formed when absolute alcohol is placed in contact with chlorocarbonic acid gas. It appears as an oily liquid, of Sp. G. 1·133, boiling at 200°. It is formed as follows: 2 eq. of chlorocarbonic acid and 1 of alcohol, losing 1 eq. hydrochloric acid, yield 1 eq. of the new ether. $C_2O_2Cl_2 + C_4H_6O_2 = HCl + C_6H_5ClO_4$. It may be viewed as a compound of oxide of ethyle, with a peculiar acid $C_2\left\{\begin{matrix}O_3\\Cl\end{matrix}\right.$; or as carbonic ether C_5H_5O, *plus* 1 eq. chlorocarbonic acid $C\left\{\begin{matrix}O\\Cl\end{matrix}\right.$.

2. *Urethane*, Syn. *Carbamate of oxide of ethyle; carbamic ether*, $C_6H_7NO_4$, is formed by the action of ammonia on the preceding compound, along with sal ammoniac, from which it is separated by being sublimed, or rather distilled, when it passes over at a gentle heat, as a liquid which crystallises on cooling. It is very soluble in water and alcohol, and yields very large crystals. It may be viewed as chlorocarbonic ether, in which amide, NH_2, has been substituted for the chlorine: $C_4H_5, O + C_2\left\{\begin{matrix}O_3\\NH_2\end{matrix}\right.$. It is formed as follows: $C_6H_5ClO_4 + 2NH_3, = (NH_3, HCl) + C_6H_7NO_4$. Berzelius, with much probability, considers it as a compound of oxide of ethyle with an acid, not yet known in the separate form, containing the elements of carbonic acid and carbamide, just as oxamic acid does those of oxalic acid and oxamide. On this view its rational formula will be

$$\underbrace{C_4H_5O}_{\text{Oxide of ethyle.}} + \underbrace{CO_2, CONH_2}_{\text{Carbamic acid.}} = C_6NH_7O_4.$$

It is remarkable that two other compounds, quite distinct in properties, have the same empirical formula as urethane or carbamic ether. These are, *lactamide,* or anhydrous lactate of ammonia $C_6 H_4 O_4 + N H_3$; and *sarcosine,* $C_6 N H_7 O_4$, a new base, derived from kreatine. (See Artificial Alkaloids.)

METAMORPHOSES OF THE COMPOUNDS OF ETHYLE.

When ether or alcohol is passed in vapour through a red hot tube, it yields aldehyde, water, olefiant gas, and marsh gas, $3 (C_4 H_5 O) = C_4 H_4 O_2 + H O + 3 C_2 H_2 + C_2 H_4$: or $2 (C_4 H_5 O) = C_4 H_4 O_2 + C_2 H_2 + C_2 H_4$. By the action of chloride of zinc on alcohol, there are formed water, and two liquid carbo-hydrogens, $C_8 H_7$ and $C_8 H_9$, together $C_{16} H_{16}$, that is, olefiant gas, or an isomeric modification of it. Now ether and alcohol both contain the elements of water and of olefiant gas ; for alcohol is $C_4 H_6 O_2 = 2 H O + C_4 H_4$; and ether is $C_4 H_5 O = H O + C_4 H_4$.

In the manufacture of ether there occur two liquids, one of which is called *oil of wine,* which is $C_{16} H_{15}$ or very nearly the proportions of olefiant gas, according to the only analysis we have. The other is called the sweet or heavy oil of wine, and is a compound of sulphuric acid with ether, and a body having the same composition in 100 parts as olefiant gas. Sweet oil of wine is $2 S O_3 + Ae O + C_4 H_4$; and as this body, $C_4 H_4$ is called etherole, the compound is named the double sulphate of oxide of ethyle and of etherole. This latter is produced, along with sulphovinic acid, from the reaction of 4 eq. dry sulphuric acid and 3 eq. ether. $4 S O_3 + 3 Ae O = (2 S O_3, Ae O, H O) + (2 S O_3, Ae O, C_4 H_4)$. The same compound is formed when sulphovinate of lime is heated, but is accompanied by alcohol, sulphurous acid, olefiant gas, and a residue of sulphate of lime and charcoal. $2 (Ca O, Ae O, 2 S O_3) = (2 S O_3, Ae O, C_4 H_4) + H O + 2 (Ca O, S O_3)$; and again, $2 (Ca O, Ae O, 2 S O_3) = 2 (Ca O, S O_3) + 2 S O_2 + C_4 H_6 O_2 + C_2 H_2 + C_2 + 2 H O$.

The sweet oil of wine is an oily liquid, quite neutral. It boils at 536°, and has the Sp. G. 1·133. When heated with water it gives off etherole as an insoluble oil, while the liquid contains pure sulphovinic acid. When the etherole, thus separated, is exposed to cold, it deposits crystals of *etherine,* a compound isomeric with etherole and with olefiant gas.

ETHIONIC, ISETHIONIC, METHIONIC, AND ALTHIONIC ACIDS.

These acids are formed by the action of sulphuric acid on ether and alcohol under various circumstances. When anhydrous acid, $S O_3$ acts on alcohol, or when olefiant gas is absorbed by that dry acid, there is formed a compound, $2 S O_3 + C_4 H_4$, in crystals, which, when put into cold water, produce ethionic acid, $2 S O_3, C_4 H_5 O$. When this solution is heated, 2 eq. of sulphuric acid and 1 of alcohol separate from one half, and there is formed from the other half isethionic acid, $2 S O_3, C_4 H_5 O$, or rather $S_2 O_5 C_4 H_5 O_2$. Ethionate of baryta, formed by adding baryta to the acid before boiling, is $2 S O_3, C_4 H_5 O, Ba O$. From it all the other ethionates may be made. The salts of isethionic acid, like those of ethionic acid, have the same composition in 100 parts as the sulphovinates ; but as they contain hyposulphuric acid, their formula is $S_2 O_5, C_4 H_5 O_2 + M O$. They crystallise with remarkable facility. When, in acting on ether with anhydrous sulphuric acid, the mixture gets too hot, there is formed a new acid, *methionic acid*, the baryta salt of which is $S_2 C_2 H_3 O_7, Ba O$, or $S_2 O_5 C_2 H_3 O_2 + Ba O$. This acid apparently bears the same relation to oxide of methyle, $C_2 H_3 O$, as isethionic does to ether, $C_4 H_5 O$. When oil of vitriol in great excess, is heated with alcohol, olefiant gas is given off, and the residue is found to contain an acid, the salts of which have the very same composition as the sulphovinates, but differ in crystalline form. This acid is called *althionic acid*. It is highly probable that the althionates are mixtures or compounds of sulphovinates with isethionates, just as the salts of ethionic acid appear to contain sulphovinates and isethionates or compounds isomeric with these. The two compounds which seem to be distinct and independent are sulphovinic acid, ($Ae O, H O, 2 S O_3$) and isethionic acid, isomeric with it, but probably arranged as ($H O, Ae O_2, S_2 O_5$) ; the salts of the former being strictly double sulphates of ethyle and bases ($M O, S O_3 + Ae O, S O_3$) ; and those of the latter being $M O + (Ae O_2, S_2 O_5)$. Whatever explanation may be given of the fact, it is a fact, that the ethionic and althionic acids and their salts have the same empirical composition as these two acids and their salts, at least acording to the best analyses we have.

PRODUCTS OF THE OXIDATION OF ETHYLE AND ITS DERIVATIVES.

The oxidation of alcohol and of ether may be effected in a great variety of ways, and the products are rather numerous, varying according to the amount of oxygen taken up. Thus we have, first aldehyde, then acetic acid, formic acid, oxalic acid, and finally carbonic acid and water. The first effect of oxidation is to destroy the radical ethyle, giving rise to a new and less complex radical *acetyle* = C_4H_3. Afterwards we obtain compounds of the still less complex radical, *formyle*, = C_2H_3, and lastly, compounds of the simple radicals carbon and hydrogen.

We shall here consider, first, the radical acetyle and its compounds: bearing in mind that, while derived from the basic radical ethyle, acetyle has no basic characters whatever, but is, on the contrary, a most distinctly acidifiable radical.

XVII. ACETYLE. C_4H_3=Ac.

Acetyle is unknown in a separate form, but is easily obtained in the form of hydrated protoxide, or *aldehyde*, and hydrated peroxide, or *acetic acid.*

1. Hydrated Oxide of Acetyle, or Aldehyde. $(C_4H_3)O,HO. = AcO,HO.$

Aldehyde is formed when ether or alcohol is passed through a red-hot tube, or when ether or alcohol are oxidised by nitric acid, or by chlorine, &c. In these cases it is not pure; but it may be obtained quite pure by distilling 2 parts of the compound of aldehyde and ammonia dissolved in 2 parts of water, along with a mixture of 3 parts of oil of vitriol and 4 of water, and rectifying at a temperature of about 80°, over chloride of calcium.

It is a clear, colourless liquid, of a peculiar and powerful etherial odour, of Sp. G. 0·79 at 65°, and boiling at 70°. It mixes in all proportions with water, alcohol, and ether, and is neutral and inflammable. In contact with the atmosphere it rapidly absorbs oxygen, passing into hydrated acetic acid: for $C_4H_3, O + HO$, with O_2, at once produce $C_4H_3, O_3 + HO$; or $AcO, HO + O_2 = AcO_3, HO$. Aldehyde is a constant ingredient of the nitrous ether of the pharmacopœias.

When heated with caustic potash, it is rapidly converted into the brown matter called resin of aldehyde. If gently heated with oxide of silver and water, part of the oxide is reduced without effervescence, coating the glass tube with a bright surface of silver, while the water is found to contain a salt of silver, the acid of which contains less oxygen than acetic acid: this is aldehydic or lampic acid, $C_4H_3O_2$, HO, or AcO_2, HO. The solution of aldehydate of silver, if filtered and heated to boiling, again deposits metallic silver, while the aldehydic acid becomes acetic.

When long kept, even in sealed tubes, aldehyde is transformed into two isomeric modifications, namely, *metaldehyde*, a hard crystalline inodorous solid, and *elaldehyde*, which is liquid.

Aldehydite of ammonia. SYN. *Aldehydammonia.* C_4H_3, $O + NH_3 + HO$. Aldehyde has no basic characters, and rather exhibits a tendency to the acid character, in combining with ammonia, as it does directly, to form a crystallised compound. To prepare it, as the substance from which aldehyde is obtained, 6 parts of oil of vitriol, 4 of water, 4 of alcohol, and 6 of peroxide of manganese, in fine powder, are distilled together. The crude product is twice rectified over chloride of calcium; it is now aldehyde, containing a little water, alcohol, and acetic and formic ethers; and this liquid, when mixed with ether, and saturated with ammoniacal gas, yields crystals of the new compound, which are washed with ether. These crystals become brown on being kept, even in close vessels, and acquire the smell of burnt feathers. They dissolve in water and alcohol, but hardly in ether. Nitrate of silver forms, in the concentrated solution, a precipitate, insoluble in alcohol, which, when heated, is reduced.

Thialdine. Liebig and Wöhler have very recently discovered that when an aqueous solution of aldehydammonia is acted on by sulphuretted hydrogen, a little ammonia being previously added, crystals of a new compound are deposited, which has basic properties, and has been called *Thialdine.* It is produced by the action of 3 eqs. of aldehydammonia on 6 eqs. of sulphuretted hydrogen. Thus—

$$\begin{array}{ll}
\text{3 eqs. aldehydammonia . . } & C_{12}\,H_{21}\,N_3\,O_6 \\
\text{and 6 eqs. sulphuretted hydrogen . } & \quad\;\, H_6 \qquad\quad S_6 \\
\cline{2-2}
 & C_{12}\,H_{27}\,N_3\,O_6\,S_6 \\
\\
\text{yield 1 eq. Thialdine . . . . } & C_{12}\,H_{13}\,N\;\; S_4 \\
\text{6 eqs. water . . . . . } & \quad\;\, H_6 \qquad\quad O_6 \\
\text{2 eqs. sulphuret of ammonium} & \quad\;\, H_8\;\; N_2\,S_2 \\
\cline{2-2}
 & C_{12}\,H_{27}\,N_3\,S_6\,O_6
\end{array}$$

Thialdine is almost insoluble in water, but very soluble in alcohol and ether. It is deposited, by spontaneous evaporation, from its etherial solution, in large and beautiful crystals, resembling camphor. It is very volatile and fusible, has an unpleasant aromatic smell, and is a powerful base, neutralising the strongest acids, and forming beautiful crystalline salts. When heated with hydrate of lime, thialdine yields *leucoline* or *quinoline,* one of the volatile bases of coal tar.

When aldehydammonia is acted on by seleniuretted hydrogen, an analagous basic compound, *selenaldine,* is formed; and it appears probable, from the experiments of Liebig and

Wöhler, that telluretted hydrogen is capable also of yielding a similar compound.

2. Acetal. $C_8 H_9 O_3 = C_4 H_3, O + C_4 H_5, O + HO = Ae\,O + Ae\,O + HO.$

Is formed by the action of the oxygen of the air on the vapours of alcohol, under the influence of the black powder of platinum. It is a colourless very mobile liquid, Sp. G. 0·825, boiling at 203°. It might, according to its composition, be a compound of 3 eq. oxide of ethyle, and 1 eq. acetic acid; for $3\,(C_4 H_5, O) + C_4 H_3 O_3 = C_{16} H_{18} O_6 = 2\,(C_8 H_9 O_3)$. But the action of potash, which forms resin of aldehyde, and of oil of vitriol, which blackens and thickens it as it does aldehyde, indicate pretty certainly the presence of aldehyde; and we therefore prefer the formula above given, which makes acetal a compound of aldehyde and oxide of ethyle.

The resin of aldehyde, formed by the action of potash on aldehyde, is little known. *Elaldehyde*, an isomeric form of aldehyde, which is liquid at ordinary temperatures, but solid at 32°, has a formula exactly triple that of aldehyde, $C_{12} H_{12} O_6$. *Metaldehyde*, the other isomeric modification, which, like the preceding, spontaneously forms in aldehyde, when kept, has, no doubt, a similar relation in its formula to that of aldehyde; but its precise formula is not yet known. The density of its vapour would settle the point. It forms very hard prisms, which sublime at 248° without melting. It is worthy of notice that aldehyde, like the corresponding chlorine compound, formed by substitution, *chloral*, $C_4 Cl_3 O + HO$, undergoes very easily, and even spontaneously, these very singular metamorphoses. This indicates a relation in the constitution of these bodies which cannot be overlooked.

3. Acetylous Acid. $(C_4 H_3) O_2, HO = Ac\,O_2, HO.$

Syn. *Aldehydic Acid. Lampic Acid.* It has already been stated that this acid is obtained in combination with oxide of silver, when aldehyde is gently heated with excess of that oxide in water. The solution, when the silver has been separated by sulphuretted hydrogen, contains the acetylous acid very diluted. It is very easily decomposed, especially by heat, into acetic acid and a brown resin, like that of aldehyde. When the acetylite or aldehydate of silver is decomposed by baryta, so as to precipitate all the oxide of silver, and the acetylite of baryta is now heated with the precipitated oxide of silver, the metal is reduced, and *acetate* of baryta is now found in the solution. This demonstrates the relation of acetylous to acetic acid: for $Ba\,O, Ac\,O_2 + Ag\,O = Ba\,O,$

$Ac\,O_3 + Ag$. This acid is one chief ingredient of the acid produced by the slow combustion of ether in the lamp with a spiral of platinum wire on the wick, the platinum continuing red-hot, but no flame appearing, and which acid is called lampic acid.

4. Acetic Acid. $C_4\,H_3, O_3 + H\,O = Ac\,O_3, HO$.

Syn. *Acetylic acid.—Pyroligneous acid.—Vinegar.*—This important acid is formed in two principal ways: first, by the oxidation of alcohol; and, secondly, by the destructive distillation of wood. Wine, beer, and other fermented liquors, if exposed to the air, under certain circumstances, undergo what is erroneously termed the acetous fermentation; that is, they attract oxygen from the air, undergo eremacausis of the alcohol they contain, and, after a time, contain no alcohol, but in its place acetic acid; they are, in fact, converted into vinegar. The ultimate change is very simple: $C_4\,H_6\,O_2 + O_4 = C_4\,H_3\,O_3,\ 3\,HO, = AcO_3,\ HO + 2\,aq.$ But we have already seen that there are intermediate steps in the process. The first effect of the oxygen is to remove from the alcohol, or rather from the ethyle in it, 2 eq. of hydrogen, thus leaving the radical acetyle, $C_4\,H_3$, in the place of the ethyle $(C_4\,H_5)\,O,\ HO + O_2 = (C_4\,H_3)\,O,\ HO + 2\,aq.$ In this stage, alcohol is simply converted into aldehyde, while 2 eq. of water are formed. In the next stage, the hydrated protoxide of acetyle (the aldehyde), or rather the radical $C_4\,H_3$, takes up 2 additional equivalents of water, and thereby becomes acetic or acetylic acid $(C_4\,H_3)\,O,\ HO + O_2 = (C_4\,H_3)\,O_3,\ HO$.

Such being the action of the oxygen of the air on alcohol, it is obvious that the process of acetification is no fermentation, but a case of eremacausis, or slow combustion. But, as was formerly explained, the state of eremacausis is induced by contact of a body in that state or even in the state of fermentation or putrefaction, and the presence of a ferment is required to commence the process of eremacausis of alcohol. Pure alcohol, exposed to air alone, is not acetified: but if its vapour, mixed with air, come in contact with platinum powder, eremacausis is induced. Hence, if alcohol be placed in a flat basin under a bell jar, beside a small flat dish containing platinum black, the bell jar is, in a few seconds, filled with the pungent smell of aldehyde, and in an hour or two, the acetification is nearly complete. Here the platinum, by virtue of its singular power of causing gases or vapours to unite on its surface, acts as a ferment, or, as it may be called, an excitant, inducing the slow combustion, and acting as a carrier of oxygen from the air to the alcohol.

In wine or beer, there is present an actual ferment in the shape of gluten or fibrin, at least in all cases where the vinous fermentation has not decomposed the whole of the ferment. In these cases, exposure to the air for a short time causes the decomposition of the gluten, &c., to recommence, and this state of decomposition, consisting in part, no doubt, of eremacausis, being mechanically communicated in the shape of motion to the particles of alcohol, slow combustion commences, and continues till every trace of alcohol has been acetified, when the process is arrested for want of fuel, that is, of alcohol. Where, in the fermentation of wine (as sherry), or of beer (as Bavarian beer), all ferment has been destroyed or removed, these liquors do not become sour when exposed to air ; and if we wish to acetify them, we must add yeast or some other ferment. So, also, when we wish to make strong vinegar by the acetification of brandy or of whiskey, we have to add a ferment, such as yeast, and expose the mixture to a certain temperature in open vats. By carefully attending to all these principles, the process of acetification may be very much abridged. The following is the rapid process now followed on the Continent. There is made a mixture of 1 part of alcohol at 80 p. c., 4 to 6 parts of water, and $\frac{1}{1000}$ of a ferment such as vinegar, honey, or must of beer. A large, high barrel is packed with twigs or shavings of beech, previously soaked in strong vinegar, and holes are drilled in the middle and upper part of the barrel to admit a free circulation of air. The mixture is now warmed to from 75° to 80°, and made to trickle slowly upon the shavings and through the barrel, thus exposing an immense surface to the air. The temperature rises rapidly to 95° or 105°, and if a proper supply of air be given, continues at that point during the operation. When the mixture has been three or four times passed through the barrel, it is found perfectly acetified : this may take place in from 24 to 36 hours. Should the supply of fresh air, that is, of oxygen, be deficient, much aldehyde is produced, which, from its volatility, is carried off as vapour, and lost. This was long a source of great loss to the makers, and the cause could not be traced, until Liebig, by the discovery of aldehyde, explained it, and showed how to avoid the loss, by giving a due supply of air. The manufacturer now obtains, as nearly as can be expected, the theoretical quantity of vinegar from his spirits. Any aromatic substance, or essential oil, or even a trace of wood vinegar (contaminated with kreosote, &c.) will arrest the progress of acetification.

The peculiar pleasant smell of good vinegar, in addition to that of pure diluted acetic acid, is owing to the presence of acetic ether. Distilled vinegar is a tolerably pure but weak acetic acid ; but to obtain acetic acid pure and strong, we must have recourse to the salts of acetic acid, which, when distilled with moderately strong sulphuric acid, yield pure acetic acid, mixed with more or less water.

The pyroligneous acid is contaminated with pyroxylic spirit and with oil of tar. When combined with soda, lime, or oxide of lead, these salts may be easily purified by crystallisation, and by heating them so far as to expel or destroy the oily impurities. The pure salts, distilled with sulphuric acid, yield acetic acid, identical with that from true vinegar.

Hydrated acetic acid, radical vinegar, or crystallisable acetic acid, AcO_3, HO, is obtained by distilling 3 parts of dry powdered acetate of soda with 9·7 of oil of vitriol, as pure and concentrated as possible : $\frac{1}{8}$ of the acid distils over by the heat spontaneously developed in the mixture ; a gentle heat expels the rest. The product is rectified and exposed to a cold of 23° or 24°, when crystals of the hydrate are formed in a weaker liquid. The crystals are allowed to drain, and then melted, and again exposed to cold. The crystals of this second operation are generally free from all superfluous water. At temperatures below 60°, hydrated acetic is solid, at 62° or 63° it melts, forming a liquid which sometimes continues liquid at a much lower temperature, and then crystallises from some very trifling cause. The Sp. G. of the liquid is 1·063 ; it boils at 248° ; has a pungent, peculiar, but agreeable smell, and a burning acid taste. It raises a blister on the skin, and soon produces a painful sore, like a mineral acid. It is miscible in all proportions with water, alcohol, and ether. It dissolves camphor and essential oils ; and the aromatic vinegar is a solution in it of camphor, with a little oil of lemons and bergamot, &c. Strong acetic acid, in this form, is used as a diffusible stimulant, applied to the nostril in faintness or sickness. It may be used, also, externally as a very powerful rubefacient and epispastic. The hydrated acid is combustible. It is decomposed by anhydrous sulphuric acid, yielding a new acid, *sulphacetic acid :* also by chlorine, yielding, by substitution, *chloracetic acid.* The vapour of acetic acid, passed through a red-hot tube, yields carbonic acid and acetone, $C_3\ H_3\ O$: the same transformation occurs when acetic acid is heated with bases.

The salts of acetic acid are, almost without exception, soluble in water : the acetates of silver and protoxide of mercury are sparingly soluble. The formula for the neutral acetates is MO, $C_4\ H_3\ O_3$, or M, $C_4\ H_3\ O_4$. There are hardly any acid salts ;

but a considerable number of basic salts, as basic acetates of lead and copper.

Acetate of oxide of ethyle or *acetic ether*, AeO, AcO_3, is easily prepared by distilling 10 parts of acetate of soda, 16 of oil of vitriol, and 6 of alcohol. The product is rectified over lime and chloride of calcium. It may also be obtained by distilling any sulphovinate with strong acetic acid. In either case, acetic acid is brought in contact with nascent ether, and combines with it. Acetic ether is a colourless liquid, of a refreshing odour, very combustible. It boils at 165° ; its Sp. G. is 0·89. It is easily decomposed by alkalies, yielding an acetate and alcohol. Acids also decompose it. It is always present, in small quantity, in wine vinegar, which owes its flavour to this compound.

Acetate of ammonia. There is a well-known febrifuge and diaphoretic remedy called the *spirit of Mindererus*, which is a diluted solution of acetate of ammonia, formed by neutralising distilled wine vinegar with carbonate of ammonia. A more uniform preparation, although stronger than that usually employed here, is made by neutralising 6 parts of aqua ammoniæ, Sp. G. 0·96, with strong acetic acid, and adding enough water to make up 24 parts. This, being uniform, can easily be reduced if desirable. There is an acid acetate of ammonia, which forms deliquescent needles. *Acetate of potash*, $KO, Ac\ O_3$, is obtained as a fibrous crystalline mass, very deliquescent, which has a warm saline taste. It is much used as a diuretic. When heated with arsenious acid, it yields oxide of kakodyle ; a substance of most remarkable composition and characters, $C_4\ H_6\ As, O$. *Acetate of Soda* $Na\ O, Ac\ O_3 + 6\ aq.$ is formed from pyroligneous acid, and is the form in which the acid is brought in order to be purified from oil of tar. The salt is melted at a moderate heat, and roasted, then re-dissolved, filtered through charcoal, evaporated, again melted, and so on, until it becomes snow-white. 10 parts of the crystals of the salt, after the first fusion, while still slightly coloured, being distilled with 6 of oil of vitriol, yield what is called wood vinegar, sufficiently pure for use, but requiring 7 waters to reduce it to the average strength of wine vinegar. Acetates of baryta, strontia, and lime, all crystallise readily. The first is used as a test ; the last in the manufacture of acetic acid and all other acetates from pyroligneous acid. *Acetate of alumina*, $Al_2\ O_3, 3\ Ac\ O_3$, prepared by mixing solutions of alum and acetate of lead (or of baryta) is very soluble. It is much used in the above form, containing sulphate of potash, as a most valuable mordant in dyeing and calico printing.

When heated it deposits an insoluble basic salt, which adheres tenaciously to the cloth, and afterwards combines firmly with the colouring matter. The pure acetate of alumina, formed from sulphate of alumina and acetate of baryta, is not so decomposed by heat, but requires the presence of a neutral salt. *Acetate of manganese*, $Mn\,O, Ac\,O_3$, formed by acting on sulphate of manganese by acetate of lime, is much used in calico printing, as it gives, with bleaching liquor, a rich bronze brown. *Acetate of zinc*, $Zn\,O, Ac\,O_3, + 3$ aq. is used in medicine and pharmacy. *Acetate of protoxide of iron*, $Fe\,O, Ac\,O_3$ is used as a mordant. *Acetate of peroxide of iron*, $Fe_2\,O_3, 3\,Ac\,O_3$, is formed by precipitating acetate of lead with persulphate of iron. It has the same valuable properties as acetate of alumina, depositing a basic salt, when heated with neutral salts, and is much prized as a mordant. *Acetate of lead; a. neutral*, Syn. *Sugar of lead;* is best prepared by dissolving litharge in acetic acid, and crystallising. It has a sweet astringent taste, and is much used as an astringent and styptic in diarrhœa, dysentery, and various hemorrhages. It is poisonous, especially where it forms carbonate : it ought therefore never to be given without abundance of vinegar being taken by the patient. The crystals are $Pb\,O, Ac\,O_3 + 3$ aq. *b. sesquibasic*, $3\,Pb\,O + 2\,Ac\,O_3$ soluble pearly scales. *c. tribasic* or *subacetate of lead* is formed in crystals by mixing 1 vol. of aqua ammoniæ with 5 of a cold saturated solution of the neutral salt, and setting it aside. It forms long needles. The solution, or Goulard's extract, is made by digesting 7 parts of litharge with 6 of sugar of lead and 30 of water, till the oxide, which is not dissolved, has become white. It is much used as a lotion, and to precipitate gum, organic acids, albumen, caseine, extractive matter, &c., from organic mixtures, and solutions. Its formula is $3\,Pb\,O + Ac\,O_3$. *d. sexbasic*, formed by adding the last or any of the previous acetates of lead to an excess of ammonia. It forms a crystalline powder; very sparingly soluble, which is $6\,Pb\,O + Ac\,O_3$. It usually exists in white lead, along with carbonate of lead.

Acetate of Copper. a. neutral; appears in two forms: as dark green oblique rhombic prisms, becoming opaque in air, $Cu\,O, Ac\,O_3 +$ aq.; and as dark blue transparent crystals of great beauty, $Cu\,O, Ac\,O_3 + 5$ aq. These latter, heated to 86°, lose 4 eq. of water, and fall to a powder of the green salt. *b. bibasic* or *verdigris*, $2\,Cu\,O + Ac\,O_3 + 6$ aq. $= Cu\,O, Ac\,O_3$, 5 aq. $+ Cu\,O, H\,O$. Verdigris is prepared by a tedious process, and is seldom pure, containing usually different basic acetates. *c. sesquibasic*, $3\,Cu\,O, 2\,Ac\,O_3 + 6$ aq. *d. tribasic*, $6\,Cu\,O$,

$2\,Ac\,O_3, + 3$ aq. The two last occur in the verdigris of commerce. All these salts are poisonous.

Schweinfurt or *Vienna green* is a double salt, formed of acetate and arsenite of copper, $Cu\,O, Ac\,O_3 + 3\,(As_2\,O_3, Cu\,O)$; is formed when 10 parts of verdigris, suspended in water, are left to digest for 24 hours, after mixing them with a hot solution of 8 parts of arsenious acid in 100 of water. A dirty green precipitate first appears, which, on standing, changes to a most beautiful green, much used as a paint.

Acetate of protoxide of mercury is obtained, in sparingly soluble silvery scales, by adding acetate of potash to protonitrate of mercury, both hot. It blackens when exposed to light. It is used in medicine, especially on the Continent.

Acetate of silver, $Ag\,O, Ac\,O_3$, very much resembles the preceding salt. It is occasionally used as a test. It is very sparingly soluble.

ACTION OF CHLORINE, BROMINE, ETC., ON ETHYLE, ACETYLE, AND THEIR DERIVATIVES.

1. Oxide of Ethyle and Chlorine.

When dry chlorine is made to act on ether, with the aid of the sun's rays, there are produced several compounds. The first is a heavy oily liquid, oxychloride of acetyle $C_4H_3 \left\{ \begin{matrix} O \\ Cl_2 \end{matrix} \right.$; which is dry acetic acid, with 2 eq. of oxygen replaced by 2 eq. of chlorine. With water, it forms acetic and hydrochloric acids. When the action is pursued, there is obtained a compound $C_4\,Cl_5\,O$, which is ether, in which all the hydrogen is replaced by chlorine. The first compound may be connected with this one by being viewed as ether in which hydrogen is partially replaced by chlorine, $C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right. O$. Finally there is obtained a crystallisable solid compound, $C_4\,Cl_6$, which may be represented as $C_4\,Cl_5$, Cl, showing that the oxygen of ether is also here replaced by chlorine. This last body is chloride of carbon, $C_2\,Cl_3$ for $C_4\,Cl_6 = 2\,C_2\,Cl_3$. Besides these compounds, there are others formed at the same time, more difficult to separate, and which are doubtless the intermediate links of the chain of substitutions, beginning with ether $C_4\,H_5$, O, and ending with *chloride of carbon*, $C_4\,Cl_5$, Cl. The other members of the series which are more easily obtained by the action of chlorine on *chloride of ethyle* (see below, p. 408), are, $C_4\,H_5$, Cl, chloride of ethyle: $C_4 \left\{ \begin{matrix} H_4 \\ Cl, \end{matrix} \right. Cl : C_4 \left\{ \begin{matrix} H_3 \\ Cl_2, \end{matrix} \right. Cl : C_4 \left\{ \begin{matrix} H_2 \\ Cl_3, \end{matrix} \right. Cl : C_4 \left\{ \begin{matrix} H \\ Cl_4, \end{matrix} \right. Cl$; and as the compound, $C_4\,Cl_5\,O$ is formed, it is probable that there is another series beginning with ether, and ending with $C_4\,Cl_5$, O, in which the oxygen remains unchanged. The above are not all cases of substitution with preservation of the type; for the compound $C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right. O$, may very likely be $C_4 H_3 \left\{\begin{matrix} O \\ Cl_2 \end{matrix}\right.$ belonging to the type of acetic acid, rather than that of ether. These compounds are as yet but little known; it is obvious that the simultaneous occurrence of so many similar compounds must render the study of them exceedingly complicated and difficult.

The body $C_4\,H_3 \left\{\begin{matrix} O \\ Cl_2 \end{matrix}\right.$, or oxychloride of acetyle, when acted on by sulphuretted hydrogen, yields two new compounds, in which its chlorine is partially or entirely replaced by sulphur. Both are crystalline: one, the oxysulphuret of acetyle, $C_4\,H_3 \left\{\begin{matrix} O \\ S_2 \end{matrix}\right.$ forms large colourless prisms: the other, oxychlorosulphuret of acetyle, $C_4\,H_3 \left\{\begin{matrix} O \\ S \\ Cl \end{matrix}\right.$, forms yellow tabular crystals.

2. Salts of oxide of ethyle with chlorine.

When chlorine acts on these salts, or ethers, their oxide of ethyle is acted on as if separate, but in many cases the acids remain combined with the new chlorinised compounds; or the acids also are acted on, and the products derived from them combine with those derived from the ether.

Acetic ether yields a compound $C_8\,H_6\,Cl_2\,O_4$, which may be viewed as $C_4\,H_3 \left\{\begin{matrix} O \\ Cl_2 \end{matrix}\right. + C_4\,H_3\,O_3$, that is, acetate of the oxychloride of acetyle. When the compound is further exposed to the action of chlorine at a high temperature, it yields a series of compounds, in which its hydrogen is gradually replaced by chlorine, till the compound $C_8\,Cl_8\,O_4$ is left, which is called perchloruretted acetic ether. Acetic ether is $C_8\,H_8\,O_4$; and we have the acetate of oxychloride of acetyle $C_8 \left\{\begin{matrix} H_6 \\ Cl_2 \end{matrix}\right. O_4$; then $C_8 \left\{\begin{matrix} H_5 \\ Cl_3 \end{matrix}\right. O_4$: $C_8 \left\{\begin{matrix} H_4 \\ Cl_4 \end{matrix}\right. O_4$: $C_8 \left\{\begin{matrix} H_3 \\ Cl_5 \end{matrix}\right. O_4$: $C_8 \left\{\begin{matrix} H_2 \\ Cl_6 \end{matrix}\right. O_4$: $C_8 \left\{\begin{matrix} H \\ Cl_7 \end{matrix}\right. O_4$: and $C_8\,Cl_8\,O_4$. The two last can be obtained, with certainty, pure: the others, after $C_8 \left\{\begin{matrix} H_6 \\ Cl_2 \end{matrix}\right. O_4$, are so mixed that it is very difficult to obtain them pure enough for analysis.

When *benzoic ether*, AeO, BzO, is acted on by chlorine, it loses 2 eq. hydrogen, and 1 eq. oxygen, and takes up 3 eq.

chlorine, producing a compound which may be viewed as containing chloride of benzoyle and oxychloride of acetyle, BzCl $+ C_4 H_3 \left\{\begin{matrix} O \\ Cl_2 \end{matrix}\right. = C_{18} H_8 Cl_3 O_3$.

Oxalic ether, exposed to the action of chlorine, under the influence of the direct rays of the sun, loses all its hydrogen, which is replaced by chlorine. $(C_4 H_5) O, C_2 O_3$ thus becomes $(C_4 Cl_5) O, C_2 O_3$. The latter is called *chloroxalic ether*. It is a crystallisable solid, fusible at 288°. Dry ammonia acts on it as on oxalic ether, producing *chloroxamethane*, a crystalline compound analogous to oxamethane. It was formerly stated that oxamethane, $C_8 H_7 NO_6$, has the composition of oxamate of oxide of ethyle $(C_4 H_5) O + C_4 H_2 NO_5$; or of oxalic ether *plus* oxamide $(C_4 H_5) O, C_2 O_3 + NH_2, C_2 O_2$. In like manner, chloroxamethane represents chloroxalic ether *plus* oxamide: $(C_4 Cl_5) O, C_2 O_3 + NH_2, C_2 O_2 = C_8 H_2 Cl_5 NO_6$. When chloroxamethane is left in contact with ammonia, it takes up 2 eq. of water, and forms a new salt, chloroxalovinate of ammonia, $C_4 Cl_5 O, NH_4 O, 2 C_2 O_3$, which is very deliquescent. From the corresponding salt of soda the chloroxalovinic acid may be obtained, which may of course be viewed as an acid oxalate of the compound $C_4 Cl_5 O$. Its formula is, $C_4 Cl_5 O, C_2 O_3 + HO, C_2 O_3$. By the action of alcohol on chloroxalic ether, there is formed a neutral oil, $C_8 Cl_5 O_7$, which contains the elements of anhydrous chloroxalovinic acid, $C_4 Cl_5 O, 2 C_2 O_3$; and when dissolved in potash, yields chloroxalovinate of potash.

Carbonic ether, by the action of chlorine, yields two products: 1st, Bichloruretted carbonic ether, $C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right. O, CO_2 = C_5 H_3 Cl_2 O_3$; and 2nd, Perchloruretted carbonic ether, $C_4 Cl_5 O, CO_2 = C_5 Cl_5 O_3$. The former is an oily liquid; the latter crystallisable.

Chloride of ethyle $(C_4 H_5) Cl$, when acted on by chlorine, yields a very remarkable series of products, in which the hydrogen is gradually replaced by chlorine, as mentioned at p. 264, to which I refer for the formulæ. I shall only here mention that the compound there represented as $C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right., Cl, = C_4 H_4 Cl_2$, corresponds to aldehyde, and is, therefore, probably $(C_4 H_3) Cl + H Cl$, just as aldehyde is $(C_4 H_3) O + HO$. In like manner, the compound $C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right., Cl = C_4 H_3 Cl_3$, corresponds to dry acetic acid, $C_4 H_3 O_3$. The action of potash on these two compounds confirms this view, according to which the former is hydrochlorate of protochloride, and the latter perchloride, of acetyle.

When *alcohol*, the hydrated oxide of ethyle, is subjected to the long-continued action of chlorine, aided by the sun's rays, there is formed, after a very tedious operation, a remarkable compound called *chloral*, the empirical formula of which is $C_4 H Cl_3 O_2 = C_4 Cl_3 O + HO$. This compound represents aldehyde or hydrated oxide of acetyle, in which the hydrogen of the acetyle has been replaced by chlorine. It is an oily liquid, boiling at 199°, of Sp. G. 1·502. Like aldehyde, chloral, when kept, is spontaneously converted into an insoluble solid compound, which has the same composition as chloral itself. In contact with water, chloral is soon converted into a solid hydrate, which dissolves in a larger quantity of water. It contains 1 eq. chloral and 2 eq. water. When heated with caustic alkalies, chloral produces formiate of the alkali and perchloride of formyle, $C_4 H Cl_3 O_2 + HO, KO = (C_2 H) O_3, KO + (C_2 H) Cl_3$. The perchloride of formyle, in contact with the alkali, is partly decomposed, yielding chloride of the metal.

According to Städeler, chloral is formed when starch is heated with hydrochloric acid and peroxide of manganese.

Pure Acetic Acid, when acted on by chlorine and the sun's rays, is converted into a crystallisable acid, the chloracetic acid, $C_4 Cl_3 O_3 HO$. As acetic acid may be considered to be aldehyde *plus* 2 eq. oxygen, or hydrated peroxide of acetyle, so chloracetic acid is chloral *plus* 2 eq. oxygen, or hydrated peroxide of $C_4 Cl_3$, which may be called *chloracetyle*. Chloracetic acid forms tabular crystals, fusible at 113°, boiling at 390°. The density of the liquefied acid at 113° is 1·617. When heated with excess of potash, it yields first carbonic acid and perchloride of formyle, $C_4 Cl_3 O_3, HO + 2 KO = 2 (KO, CO_2) + C_2 HCl_3$. The perchloride of formyle is partly converted by another portion of potash, into formiate of potash and chloride of potassium. $C_2 HCl_3 + 4 KO = 3 K Cl + KO, C_2 HO_3$.

With bases, chloracetic acid forms salts which are very analogous to the acetates; and it is very important here to observe, that both in chloral and chloracetic acid, the substitution of chlorine for all the hydrogen of the radical (acetyle) of aldehyde and acetic acid, has not affected the general chemical characters of the compounds; that, in other words, the original type has been retained. We have also seen, in the preceding pages, among the products of the action of chlorine on oxide of ethyle and on the salts of oxide of ethyle, that oxide of ethyle, $C_4 H_5 O$, is converted into oxide of chlorethyle, $C_4 Cl_5 O$, without the type being altered: the oxide of chlorethyle forming with the acids previously combined with oxide of ethyle, compounds perfectly analogous to the ethers from which they are obtained.

The *sulphuret of ethyle* is readily acted on by chlorine, and yields a yellow oily liquid, of Sp. G. 1·673, boiling at 320°, of a most fetid odour, the formula of which is $C_4 \left\{ \begin{matrix} H \\ Cl_4 \end{matrix} \right. S$. Here 4 eq. of hydrogen of the compound, $C_4 H_5 S$, are replaced by chlorine.

Heavy muriatic ether is an oily liquid, formed by the action of moist chlorine on alcohol. It is obviously a mixture, and probably contains aldehyde, chloride of ethyle, chloral, and products intermediate between aldehyde and chloral.

Bromal. $C_4 Br_3 O, HO$. This compound, analogous to chloral, is formed by the action of bromine on alcohol. It forms a hydrate with 3 eq. water. By caustic alkalies it is resolved into formic acid, which combines with the alkali, and perbromide of formyle.

Iodine does not, so far as is known, produce a compound corresponding to chloral and bromal; but a solution of iodine in alcohol, treated with an alcoholic solution of potash, yields formiate of potash and peroxide of formyle, $C_2 H I_3$.

By the action of chlorine on alcohol, holding in solution hydrocyanic acid on a metallic cyanide, there is produced a crystalline compound, the empirical formula of which appears to be $C_{16} H_{14} N_2 Cl_2 O_8$. This is equal to 3 eq. aldehyde, 2 eq. chloride of cyanogen, and 2 eq. water; but the true nature of this compound is unknown.

3. Compounds derived from Alcohol, but of uncertain constitution.

Olefiant Gas. Syn. *Hyduret of Acetyle.* $C_4 H_4 = C_4 H_3, Cl = AcH$. This well-known compound is generally present in coal gas, oil gas, and, in general, in all gaseous mixtures produced by the action of heat on organic substances. It is best obtained pure by heating 1 part of alcohol with 6 or 7 of oil of vitriol. There is produced some ether, then sweet oil of wine, and lastly, a mixture of sulphurous acid and olefiant gases. By passing the gas through milk of lime, the sulphurous acid is removed, and by then passing it through oil of vitriol, the ether, alcohol, and water which may be present, are likewise separated. Pure olefiant gas has been already described (see p. 128, Part I.): here we shall attend to its combinations. It is absorbed by anhydrous sulphuric acid, forming the crystalline compound formerly mentioned, $2 SO_3 + C_4 H_4$, which, in contact with water, produces ethionic acid. When mixed with its own volume of chlorine, both gases are condensed into a liquid, the composition of which is $C_4 H_4 Cl_2$. This is the oily compound, from which the gas was called olefiant gas: the oil is often called the oil of the Dutch chemists, having been discovered by an association of chemists in olland.

When mixed with 2 vol. of chlorine, and set fire to, the whole of the carbon of the gas is deposited in the solid form or as smoke, while all the hydrogen forms hydrochloric acid, $C_4 H_4 + Cl_4 = 4 H Cl + C_4$.

The oil of olefiant gas, or of the Dutch chemists, $C_4 H_4, Cl_2$, may be viewed as composed of hydrochloric acid, and a chloride of acetyle; $H Cl + C_4 H_3 Cl$. When acted on by an alcoholic solution of potash, chloride of potassium and water are formed, and a new compound separates, which is the *protochloride of acetyle*, $C_4 H_3 Cl$. It is gaseous at ordinary temperatures, has an alliaceous smell, and burns, like all similar chlorinised compounds, with a dark red flame edged with green. At 0° it condenses into a liquid.

When this protochloride of acetyle is acted on by perchloride of antimony, it yields, among other products, a liquid, boiling at 240°, which is $C_4 H_3 Cl_3$, and therefore has the same composition as perchloride of acetyle, formerly mentioned. But the action of potash, dissolved in alcohol, proves that these two compounds are distinct, and that the one now under consideration is $C_4 H_2 Cl_2 + H Cl$. At all events, it yields chloride of potassium, water, and a very volatile liquid, $C_4 H_2 Cl_2 = 2 (C_2 H, Cl)$, or in other words, protochloride of formyle.

By continuing the action of chlorine there is obtained a compound $C_4 H_2 Cl_4 = C_4 H Cl_3 + H Cl$; which, with potash, yields the body $C_4 H Cl_3$; and the final result of this action is the protochloride of carbon, $C_4 Cl_4 = 4 C Cl$; which, however, unites with chlorine to produce the sesquichloride, $C_4 Cl_4 + Cl_2 = C_4 Cl_6 = 2 C_2 Cl_3$.

The *perchloride of acetyle* has been already mentioned as a product of the action of chlorine on ether: it is $C_4 H_3 Cl_3 = Ac Cl_3$.

The oil of olefiant gas, $C_4 H_4 Cl_2$, which may be considered the hydrochlorate of chloride of acetyle, $C_4 H_3, Cl + H Cl$, is best prepared by passing olefiant gas into perchloride of antimony, as long as it is absorbed. The mixture, if distilled, yields the oil in question. It is purified by alternate distillation with water and sulphuric acid, and finally drying it with chloride of calcium. It is a very mobile liquid, of a pleasant etherial smell, and a very sweet taste; it boils at 180°, is insoluble in water, soluble in alcohol and ether.

When subjected to the action of chlorine, it yields hydrochloric acid, and products rich in chlorine. Among these are, the hydrochlorate of chloride of formlye, $C_2\ H\ Cl + H\ Cl$, which distils at 240°, and the bichloride of formyle, $C_2\ H,\ Cl_2$, which distils at 275°. This last is finally converted into sesquichloride of carbon; for $C_2\ H,\ Cl_2 = C_2\ Cl_2 + H\ Cl$.

Chloretheral is the name given by D'Arcet to a compound formed by the action of chlorine on olefiant gas, containing both alcohol and ether. Its empirical formula is $C_4\ H_4\ Cl\ O$; so that it may be aldehyde, *plus* oil of olefiant gas; $C_4\ H_3\ O,\ HO + C_4\ H_3\ Cl,\ H\ Cl = 2\ (C_4\ H_4\ Cl\ O)$; or oxychloride of acetyle, *plus* oxide of ethyle: $C_4\ H_3 \left\{ \begin{matrix} O \\ Cl_2 \end{matrix} \right. + C_4\ H_5\ O = 2\ (C_4\ H_4\ Cl\ O)$. The true nature of this compound is unknown.

Bromine forms, with olefiant gas, a liquid compound analogous to the oil of olefiant gas. Its formula is $C_4\ H_3,\ Br + H\ Br$. Iodine forms, with olefiant gas, a solid compound, which would appear to be $C_4\ H_3,\ H + I_2$ rather than $C_4\ H_3,\ I + H\ I$.

Anhydrous sulphuric acid absorbs olefiant gas, producing a white crystalline solid, $2\ S\ O_3 + C_4\ H_4$; which, when dissolved in water, forms with 1 eq. of water, ethionic acid, $2\ S\ O_3 + C_4\ H_5\ O = C_4\ H_5\ O_2 + S_2\ O_5$. The original crystalline compound has been called sulphacetylic acid.

4. Action of Bichloride of Platinum on Alcohol.

This action is very complex, yielding aldehyde, chloride of ethyle, chloride of acetyle, and other volatile compounds, along with a salt, composed of chloride of platinum and chloride of acetyle. It is possible that 3 eq. of oxide of ethyle, with 4 eq. of bichloride of platinum, may yield 1 eq. aldehyde, 1 eq. water, 4 eq. hydrochloric acid, and 2 eq. of the new salt. $3\ (C_4\ H_5\ O) + 4\ Pt.\ Cl_2 = C\ H_3\ O,\ H\ O + H\ O + 4\ H\ Cl + 2\ (C_4\ H_3\ Cl + Pt_2\ Cl)$. Zeise considers the salt to be $C_4\ H_4 + 2\ Pt\ Cl$, which formula differs from the preceding in containing 1 eq. hydrogen more. Malaguti supposes it to be $C_4\ H_3\ O + 2\ Pt\ Cl$; but Zeise has shown that it contains no oxygen. It does not crystallise, but forms a gummy mass, spontaneously decomposing when kept.

When a solution of bichloride of platinum in alcohol is digested with a little hydrochloric acid, and chloride of potassium, the alcohol distilled off, and the residue neutralised by carbonate of potash, a yellow crystallisable salt is obtained, which contains the preceding compound, plus 1 eq. chloride of potassium, $C_4\ H_3\ Cl + Pt_2\ Cl + K\ Cl$. Similar double salts are formed with chloride of sodium and chloride of ammonium.

These double salts form with ammonia a yellow precipitate, which is $C_4 H_3 Cl, Pt Cl + N H_3$.

5. Action of Heat on Acetic Acid and the Acetates.

Acetone,—Syn. *Pyroacetic Spirit. Mesitic Alcohol.* Formula $C_3 H_3 O$,—is formed when acetic acid is passed through a tube heated to low redness, along with carbonic acid, carbonic oxide, and carburetted hydrogen: also when the acetate of an alkali or alkaline earth is exposed to heat, when a carbonate is left, and acetone distils over. It is best prepared by distilling a mixture of 2 parts of crystallised acetate of lead, and 1 part quicklime. Its formation is easily explained; for anhydrous acetic acid, $C_4 H_3 O_3$, contains the elements of 1 eq. carbonic acid, and 1 eq. acetone. $C_4 H_3 O_3 = CO_2 + C_3 H_3 O$. Acetone is also formed in the distillation of sugar, of citric acid, of tartaric acid, &c. It is purified by rectification, until its boiling point becomes constant, at 100°. It is a clear and colourless liquid, of Sp. G. 0·7921, and has a peculiar smell and a pungent taste. It is miscible with water, alcohol, and ether, in all proportions ; and is separated from water by the addition of caustic potash, chloride of calcium, or other salts insoluble in acetone.

Heated with hypochlorite of lime, it is converted into carbonic acid and perchloride of formyle. When prepared by the distillation of acetates, acetone is accompanied by an oily liquid, $C_{10} H_8 O$.

Acetone contains, in 3 eq., the elements of 1 eq. carbonic ether and 1 eq. olefiant gas (hyduret of acetyle). $C_4 H_5 O, CO_2 + C_4 H_3, H = C_9 H_9 O_3 = 3 (C_3 H_3 O)$; or, in 4 eq.: we have the elements of 1 eq. acetic ether, and 1 eq. hyduret of acetyle : $C_4 H_5 O, C_4 H_3 O_3 + C_4 H_3, H = C_{12} H_{12} O_4 = 4 (C_3 H_3 O)$. Kane considers acetone to be $C_6 H_6 O_2 = C_6 H_5 O, H O$; that is, the hydrated oxide of a radical $C_6 H_5$, which he calls *mesityle*. In this view, acetone is analogous to alcohol, and $C_6 H_5 O$, the oxide of mesityle, to ether. But although Kane has obtained this compound, $C_6 H_5 O$, and also another, $C_6 H_5 Cl$, his chloride of mesityle, and although he has likewise formed double salts containing sulphuric acid and the elements $C_6 H_5 O$, yet the analogy is far from being established. It has not yet been found possible to reproduce acetone, the *alcohol*, from the supposed *ether* of the series, as we can reproduce alcohol from the salts of oxide of ethyle. Moreover, in these double salts, the body $C_6 H_5 O$, does not act as a base, but is only coupled with the acid, as naphthaline in sulphonaphthalic acid. We shall not, therefore, enter into minute details of the theoretical views alluded to. It is sufficient to enumerate the supposed radical *mesityle*, $C_6 H_5$; its oxide, $C_6 H_5 O$, oxide of mesityle ; its hydrated oxide, $C_6 H_5 O, H O$ (acetone) ; the chloride and iodide of mesityle, $C_6 H_5 Cl$ and $C_6 H_5 I$; the acid sulphate of oxide of mesityle, $C_6 H_5 O, H O, 2 S O_3$ (sulphomesitylic acid) ; the double salts of this sulphate, the formula of which is $C_6 H_5 O, H O, 2 M O, 2 S O_3$; and a compound discovered by Zeise, containing oxide of mesityle with chloride of platinum, $C_6 H_5 O, Pt Cl$.

The action of nitric acid on acetone gives rise to a new product : *nitrite of oxide of pteleyle*, $C_6 H_3 O, N O_3$; phosphoric acid appears to form a compound acid with acetone ; and when phosphorus, iodine, and acetone are distilled together, another acid is obtained, which appears to contain hypophosphorous acid.

When chlorine acts on acetone, it produces a liquid, $C_6 H_4 Cl_2 O_2$, which is called *mesitic chloral.*

Mesitylene, $C_6 H_4$. This compound is obtained when acetone is distilled with fuming sulphuric acid. It is an oily liquid, boiling about 300°. Acetone $2 (C_3 H_3 O) = C_6 H_4 + 2 H O$; and this explains its production.

When mesitylene is acted on by nitric acid, it yields a liquid, $C_6 H_4 O_2$, called by Kane mesitic aldehyde. But when chlorine is passed through mesitylene, a crystalline solid is obtained, containing a new radical pteleyle, combined with chlorine, $C_6 H_4 + Cl_2 = C_6 H_3 Cl + H Cl$. The compound $C_6 H_3 Cl$ is the chloride of the supposed new radical pteleyle, $C_6 H_3$. Kane has described a compound in yellow scales, which he considers to be iodide of pteleyle. It is very desirable that the whole of the compounds derived from acetone should be again carefully examined, since their true constitution cannot be considered as established.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETYLE.

When acetate of potash is heated along with arsenious acid, a very remarkable liquid is obtained, which is the oxide of a new radical. This liquid, which is spontaneously inflammable, and has a most offensive alliaceous smell, has been long known in an impure state, under the names of the liquor of Cadet, and *alcarsine.* Bunsen, by a long series of the most profound and persevering researches, established its true character as the oxide of the radical *kakodyle.* He has even succeeded in obtaining the radical itself in the separate state, and in establishing the most perfect analogy between that radical and a metal, in all its chemical relations.

XVIII. Kakodyle. $C_4 H_6 As = Kd$.

The radical is best obtained from the chloride of kakodyle, $Kd\,Cl$, by the action of zinc at 212°. Chloride of zinc is formed, and kakodyle is set free. It is rectified in an apparatus filled with carbonic acid gas, to prevent decomposition. It is a clear liquid, refracting light strongly. When cooled, it crystallises in large square prisms, and acquires, when pure, the appearance of ice. Its smell is insupportably offensive, and its vapour is highly poisonous. The two latter characters belong to all the compounds of kakodyle, with hardly an exception. Kakodyle is spontaneously inflammable in the air; a rod moistened with it instantly takes fire when exposed to the air. It forms two distinct oxides: the protoxide, $Kd\,O$ (alkarsine), and kakodylic acid, $Kd\,O_3$.

Protoxide of Kakodyle. $C_4 H_6 As, O = Kd\,O$.

Syn. *Alkarsine.* This is the chief ingredient of the liquor of Cadet; it is purified by repeated rectifications in an atmosphere of carbonic acid, and is, when pure, a limpid etherial liquid, refracting light powerfully; it boils at about 300°, and at—9° it crystallises in white scales of a satiny lustre. Its smell is most offensive, and its taste very nauseous. If placed on the skin, it causes violent itching, and if taken internally it is a most energetic poison. It is sparingly soluble in water, more soluble in alcohol and ether. Like kakodyle, it takes fire when exposed to the air. When left under water, it gradually disappears, being for the most part converted into kakodylic acid. The production of oxide of kakodyle is very simple: 2 eq. dry acetic acid and 1 eq. arsenious acid yield 4 eq. carbonic acid and 1 eq. oxide of kakodyle. $2\,(C_4\,H_3\,O_3) + As\,O_3 = 4\,C\,O_2 + C_4\,H_6\,As\,O$.

Kakodylic Acid. $Kd\,O_3 = C_4 H_6 As, O_3$.

Syn. *Alcargene.* Formed by the gradual oxidation of the protoxide, under water. It forms oblique four-sided prisms, brittle, and of a glassy lustre. They have no smell, and are soluble in water and alcohol. Its salts do not crystallise. Many reducing agents convert it into the protoxide by removing 2 eq. of oxygen. It is not in the least poisonous.

There appears to be an intermediate oxide, $Kd\,O_2$; but it has not been obtained in a state of purity.

Chloride of Kakodyle, $Kd\,Cl = C_4\,H_6\,As, Cl_4 = Kd\,Cl$, is obtained by heating a compound of oxide of kakodyle and corrosive sublimate along with hydrochloric acid: $Kd\,O$,

$Hg\,Cl_2 + H\,Cl = Kd\,Cl + HO + Hg\,Cl_2$. It is a volatile, horribly fetid liquid, the vapour of which attacks strongly the lining membrane of the nose, and provokes a flow of tears. When exposed to the air, it deposits crystals of an oxychloride of kakodyle $Kd\,O + 3\,Kd\,Cl$. The iodide, bromide, and fluoride of kakodyle, are in all points analogous to the chloride; and form, when exposed to the air, oxyiodide, oxybromide, &c.

Sulphur forms with kakodyle three compounds; the *protosulphuret*, $Kd\,S$, is obtained by distilling chloride of kakodyle with hydrosulphuret of sulphur of barium: $Kd\,Cl + Ba\,S, HS = Kd\,S + Ba\,Cl + HS$. It is a clear, volatile, very fetid liquid, heavier than water. It dissolves sulphur, forming the *bisulphuret* $Kd\,S_2$, which is a very permanent compound The *persulphuret*, $Kd\,S_3$ is a sulphur acid, and forms sulphur salts which are very permanent, with the sulphurets of highly basic metals. The sulphur salt of kakodyle and lead, $Pb\,S, Kd\,S_3$, crystallises beautifully.

Cyanide of Kakodyle, $Kd\,Cy = C_4\,H_6\,As, C_2\,N$, is formed by distilling bicyanide of mercury with water and oxide of kakodyle. When pure it forms large brilliant crystals, very fusible and volatile. The vapour of this compound is so poisonous as to be in the highest degree dangerous to the experimenter.

COMPOUNDS OF KAKODYLE CONTAINING PLATINUM.

Chloride of Kakoplatyle, $C_4\,H_7\,As\,Pt\,O_2, Cl$. This compound is formed when an alcoholic solution of bichloride of platinum is added to a similar solution of chloride of kakodyle, when a reddish-brown precipitate is formed, which, being boiled with water, gives a solution from which, on cooling, needles of the new compound are deposited. *Bromide of kakoplatyle* and *iodide of kakoplatyle* may be formed from the chloride, and are analogous to it. The former appears in large yellow crystals, the latter in golden micaceous scales.

When the chloride is acted on by sulphate of silver, there is obtained, along with chloride of silver, the sulphate of the oxide of kakoplatyle, $C_4\,H_7\,As\,Pt\,O_3, SO_3$. It forms white crystalline grains.

The radical of these singular compounds, kakoplatyle, may be represented as composed of protoxide of platinum, water, and kakodyle; $Pt\,O, HO, C_4\,H_6\,As_2$. We have therefore the following series, which, like those derived from the bases containing platinum, formerly described, throws much light on the nature of the vegetable bases.

Radical, Kakoplatyle	$Pt\,O + Kd$	$= C_{14} H_6 As\,Pt\,O.$
Chloride of do., anhydrous	$Pt\,O, Kd + Cl$	
Chloride, hydrated	$Pt\,O, Kd + Cl + H\,O$	
Chloride, ammoniated	$Pt\,O, Kd + Cl + N\,H_3$	
Oxide, hydrated	$Pt\,O, Kd + O + H\,O$	
Sulphate, hydrated	$(Pt\,O, Kd + O, H\,O) + S\,O_3.$	

It is to be particularly borne in mind that this radical, whose basic character is quite obvious, contains two metals, arsenic and platinum, quite foreign, in general, to organic compounds.

The existence of kakodyle itself, and the perfect analogy which may be traced between it and the simple metals, in their relations to all other substances, render the results of the researches of Bunsen, which have been so very briefly described in this work, of the very highest importance to the theory of organic compounds, and especially to that of compound radicals.

APPENDIX TO ETHYLE AND ACETYLE.—SUGAR.

Sugar, as the substance from which alcohol and all the compounds of ethyle are exclusively obtained, comes properly to be considered here as an appendix to these compounds. There are several kinds of sugar, capable of undergoing fermentation and of producing alcohol. These are, cane sugar; grape sugar; (sugar of starch; of honey; diabetic sugar); sugar of milk; and uncrystallisable sugar. The sugar of mushrooms has been found to be mannite, which is not fermentescible.

1. *Cane sugar*, $C_{12} H_9 O_9 + 2\,HO$, occurs in great abundance in the sugar-cane, the beet-root, the maple, besides many other vegetables. It is extracted from the juice of these plants by crystallisation, the evaporation being conducted at as low a temperature as possible. It crystallises with great facility, either in small grains by rapid cooling of a strong syrup, as in loaf sugar; or in large distinct crystals by a slow process, as in sugar candy. The above formula represents the composition of pure crystallised sugar.

Sugar forms large transparent hard crystals, which melt at 302°, or, according to Peligot, at 356°, forming a viscid liquid, which on cooling forms a transparent amorphous mass, *barley sugar*. This, when kept, gradually becomes crystalline, opaque, and friable. About 420° sugar is converted into a brown tasteless mass, *caramel*, losing 3 eq. of water.

Sugar dissolves in $\frac{1}{3}$ of its weight of cold, and in any quantity of boiling water; a solution saturated at 230° becomes a solid crystalline mass on cooling (tablet): a solution saturated in the cold is viscid, and is called syrup. Syrup, when long boiled, loses the property of crystallising. The crystallisation of sugar from syrup is also prevented by the addition of $\frac{1}{30}$ of oxalic, citric, or malic acids. When boiled with diluted sulphuric acid, cane sugar is converted into grape sugar. With strong sulphuric acid it produces a dark brown liquid, containing a new acid, sulphosaccharic acid. Nitric acid converts it into saccharic acid, oxalic acid, and carbonic acid.

When boiled with very diluted sulphuric acid, sugar absorbs oxygen from the air, and produces formic acid, and a brown matter identical with ulmine, formed by the decay of wood. Sugar prevents the precipitation of many metallic solutions by alkalies ; and when mixed with oxide of copper and potash, the oxide of copper is dissolved, forming a purple solution, which, on boiling, deposits red suboxide of copper. It reduces partially the oxides of many metals, when boiled with their solutions.

Sugar forms crystallisable compounds with the alkalies, oxide of lead, and chloride of sodium. When in contact with the lining membrane of the stomach of a calf, or with the caseine of milk, sugar is transformed into lactic and butyric acids.

Sugar, if taken along with nitrogenised food, may be called nutritious : it would appear, however, to act chiefly in contributing to the support of respiration, and thus keeping up the animal heat. An animal, confined to sugar as food, soon dies from want of nitrogenised or albuminous matter, with the symptoms of starvation.

When a solution of sugar is examined by polarised light, it gives rise to a series of rings of the prismatic colours, when the plane of polarisation is made to rotate from left to right.

SUGAR WITH BASES AND SALTS.

With lime sugar forms a sparingly soluble compound, $C_{12} H_9 O_9 + \left\{\begin{matrix} Ca\,O \\ HO \end{matrix}\right.$. With baryta, it forms a crystallisable compound, $C_{12} H_9 O_9 \left\{\begin{matrix} Ba\,O \\ HO \end{matrix}\right.$. With oxide of lead it yields an insoluble compound, $C_{12} H_9 O_9, 2\,Pb\,O$; and with common salt it yields a crystalline compound, $2\,C_{12} H_9 O_9 + \left\{\begin{matrix} 3\,HO \\ Na\,Cl \end{matrix}\right.$

2. *Grape Sugar.* Syn. *Glucose. Diabetic Sugar. Starch-Sugar*, $C_{12} H_{14} O_{14}$. This sugar occurs in the juice of many fruits, and is besides a product of the metamorphosis of starch, cane sugar, woody fibre, sugar of milk, &c., when boiled with diluted acids. It may also be obtained from starch by the action of infusion of malt, or of diastase. It occurs in the

urine of those affected with *diabetes mellitus.* The crystals which form in honey are likewise grape sugar.

It is best extracted from *dried grapes*, or honey, and is also prepared on the large scale from starch. 1 part of starch is boiled with 4 of water, and from $\frac{1}{100}$ to $\frac{1}{10}$ of sulphuric acid, during 36 or 40 hours; or an infusion of malt is added to jelly of starch, which soon becomes liquid, and, in a few hours, is converted into sugar. When acid is used, it is neutralised by chalk, the solution of sugar filtered, and evaporated to a syrup, or, if required, to a dry mass. In this process, starch, $C_{12}H_{10}O_{10}$, takes up 4 eq. water, and produces grape sugar $C_{12}H_{14}O_{14}$; so that 100 parts of pure starch yield, or ought to yield, 122 of grape sugar. The same explanation, only varying the quantity of water, applies to the conversion into grape sugar of cane sugar, $C_{12}H_{11}O_{11}$; woody fibre, $C_{12}H_8O_8$; and sugar of milk, $C_{12}H_{12}O_{12}$, these compounds requiring 3, 6, and 2 eq. of water respectively to form grape sugar.

The action of infusion of malt is not explained: all that we know is, that this infusion, or a solution of diastase, a substance contained in it, do actually cause starch to take the form of grape sugar. It is probable that the diastase is in a state of decomposition, and may act as a ferment. The action of the acid would seem to be equally obscure; but there is some reason to think that there is first formed, as in the case of ether, a coupled acid, or acid salt, which, like sulphovinic acid, is decomposed by boiling. According to De Saussure, sulphuric acid and starch actually form a crystallisable compound.

Grape sugar crystallises from alcohol in square tables or cubes: a concentrated syrup of it yields only a mass formed of crystalline grains. It is much less soluble, requiring 1½ part of cold water, and less sweet to the taste, than cane sugar: in fact, 1 part of cane sugar sweetens as much as 2½ of grape sugar. It is much more soluble in cold alcohol than cane sugar. At 212° grape sugar loses 2 eq. of water; when heated beyond 284° it becomes caramel. Hot water dissolves any quantity of grape sugar, but the syrup is not nearly so viscid as that of cane sugar. Solution of grape sugar exhibits the prismatic rays with polarised light when the plane of polarisation is rotated from right to left, the colours being less brilliant. Now, as cane sugar, when fermented, first becomes grape sugar, the coloured rings at first shown by it when the plane of polarisation is rotated from left to right disappear during fermentation, but reappear when rotation is made from right to left.

Grape sugar is easily distinguished from cane sugar by the action of acids and bases. Strong sulphuric acid dissolves without charring it, forming sulphosaccharic acid; and the alkalies or alkaline earths, which do not decompose cane sugar unless very concentrated, rapidly convert grape sugar into a brown matter. Peroxide of lead converts it, at 212°, into basic formiate of lead, carbonate of lead, and water.

With baryta and lime, and oxide of lead, grape sugar forms compounds which it is difficult to obtain pure. That with baryta appears to contain 3 eq. baryta for 2 eq. of sugar, and as the baryta replaces water in such compounds, it is probably $C_{24}H_{25}O_{25}, 3\,BaO = C_{24}H_{22}O_{22}\left\{\begin{matrix}3\,BaO\\ 3\,HO\end{matrix}\right.$. The compound with lime appears to be $C_{12}H_{12}O_{12}, 2\,CaO$; and that with lead $C_{12}H_{11}O_{11}, 3\,PbO$. If we suppose the dry grape sugar to be $C_{12}H_{11}O_{11}$, and to combine with 3 eq. water and 3 eq. base, then we should have

Crystallised grape sugar . . .	$C_{12}H_{11}O_{11} + 3\,HO$
Compound with baryta . . .	$\left\{\begin{matrix}C_{12}H_{11}O_{11} + 3\,HO\\ C_{12}H_{11}O_{11} + 3\,BaO\end{matrix}\right.$
———— lime . . .	$C_{12}H_{11}O_{11} + \left\{\begin{matrix}2\,CaO\\ HO\end{matrix}\right.$
———— oxide of lead . .	$C_{12}H_{11}O_{11} + 3\,PbO$

But the compound which grape sugar forms with common salt, and which crystallises very readily, does not agree exactly with this view. The crystals are $2\,(C_{12}H_{12}O_{12}) + NaCl + 2\,HO$; and at 212° they lose the two equivalents of water.

The sulphosaccharic acid, above mentioned as being formed when grape sugar is acted on by oil of vitriol, has not been fully examined. It forms a soluble salt with baryta.

With organic acids grape sugar forms compounds, the sugar in which cannot be brought to crystallise. Hence organic acids in vegetable juices act injuriously by first converting cane sugar into grape sugar, and then forming with it uncrystallisable compounds.

When sugar is boiled with hydrochloric acid, it yields different brown products, according to the strength of the acid. With equal parts of acid and water, it yields a body, $C_{24}H_{11}O_{9}$: with a weaker acid, two brown compounds; a soluble one, $C_{40}H_{14}O_{12}$, and an insoluble one, $C_{40}H_{16}O_{14}$. When boiled with diluted sulphuric acid, two substances are formed, which are nearly black; one, *sacchulmine*, insoluble, and the other *sacchulmic acid*, soluble in ammonia. The latter is $C_{35}H_{10}O_{15}$.

When boiled with alkalies, cane sugar is first converted into grape sugar, and then into formic acid, and two new acids, the *glucic acid* and the *melassic acid.* Glucic acid is very soluble, and its formula is either $C_{24} H_{15} O_{15}$, 6 HO, or $C_{12} H_8 O_8$, 3 HO. It is chiefly formed before the application of heat, which converts it into melassic acid. This latter acid is formed from sugar by the joint action of heat and alkalies. It has a very dark colour, and when separated by hydrochloric acid, appears as a black flocculent deposit. Its formula is $C_{24} H_{12} O_{10}$ (?).

Caramel, the black matter formed by heating sugar to about 400°, has the formula of anhydrous cane sugar $C_{12} H_9 O_9$. It dissolves readily in water, forming a solution like sepia, which is tasteless when pure. The caramel of commerce contains a good deal of undecomposed sugar.

When sugar is distilled with 3 parts of lime, it yields a liquid which is a mixture of acetone and metacetone. Metacetone is a colourless liquid, of an agreeable odour, boiling at 183°, and insoluble in water. Its formula is $C_6 H_5 O$; and it may be considered as 2 eq. acetone, $C_6 H_6 O_2$, *minus* 1 eq. water.

1 eq. of anhydrous sugar	$C_{12} H_9 O_9$
Contains—1 eq. acetone	$C_3 H_3 O$
1 eq. metacetone . . .	$C_6 H_5 O$
3 eq. carbonic acid	$C_3 O_6$
1 eq. water	$H O$
Together	$C_{12} H_9 O_9$

The formation of these products is therefore easily accounted for.

When sugar is heated with hydrate of potash, several products are formed, but among them is an acid, $C_6 H_6 O_4 = C_6 H_5 O_3$, HO, which is *metacetonic acid,* evidently derived from metacetone by oxidation at the expense of the hydrate. It is very similar to acetic acid, and, like it, belongs to the series of volatile acids of the general formula, $(CH)n + O_4$.

ACTION OF NITRIC ACID ON SUGAR.

Saccharic Acid, $C_{12} H_{10} O_{11}$, 5 HO ?, or $C_6 H_4 O_7$, HO, is one of the products of the action of diluted nitric acid on cane or grape sugar. When stronger acid is used, oxalic and carbonic acids are the chief products. When sugar has been heated with 2 parts of nitric acid and 10 of water, the acid liquid gives, with basic acetate of lead, an insoluble saccharate of lead, which is decomposed by sulphuretted hydrogen, and the acid solution so far neutralised with potash that on evaporation it yields crystals of the acid saccharate of potash. This salt is purified, again converted into saccharate of lead, and again the lead salt is decomposed by sulphuretted hydrogen. The acid this time is pure. It crystallises with difficulty.

This acid has been supposed to be quintibasic, and to form five series of salts, but the latest researches of Heintz lead to the conclusion that it is either $C_6 H_4 O_7$, HO, or $C_{12} H_8 O_{14}$, 2 HO. Owing to the very discordant results of different experimenters, we shall not here enter into details which are uncertain. Saccharic acid forms a crystallisable acid salt with potash, and definite salts with many other bases. It is isomeric with mucic acid: for $C_{12} H_8 O_{14}$, 2 HO is the probable formula of mucic acid.

The saccharate of silver, when gently heated under water, is decomposed, the silver being reduced; and as this occurs without effervescence, the reduced metal adheres to the glass, and forms a bright mirror surface. The other saccharates are only interesting in respect to their composition. On the whole, saccharic acid is a compound of high theoretical interest, and the formation of two isomeric acids, saccharic and mucic, by the action of nitric acid on cane and grape sugar on the one hand, and on sugar of milk on the other, is a fact which may hereafter lead to a knowledge of the true constitution of the different kinds of sugar.

Notwithstanding the fact that cane sugar is easily converted into grape sugar, and that the formulæ differ only by 3 eq. water, it is evident that these two kinds of sugar differ more than if they were merely different hydrates of the same compound. Strong mineral acids instantly decompose cane sugar, but have little action on grape sugar; while alkalies, which combine with cane sugar to form crystalline compounds, rapidly convert grape sugar into dark compounds, glucic and melassic acids. And although both sugars agree in undergoing the same (vinous) fermentation, yet it is most probable that cane sugar, before fermenting, becomes grape sugar.

When vegetable juices containing cane sugar are evaporated, the presence of organic acids causes its conversion into grape sugar; and when lime is added, to clarify the juice, the action of the lime on grape sugar when evaporated, produces glucic and melassic acids; in other words, renders much sugar dark and uncrystallisable, converting it into molasses. A great part of the loss owing to this cause has of late years been avoided by carefully neutralising with sulphuric acid as soon as the lime has effected the clarification.

3. *Sugar of milk, or lactine,* $C_{24} H_{19} O_{19} + 5\,HO = C_{24} H_{24} O_{24}$, is obtained by evaporating clarified whey till it

crystallises. When pure it forms hard white crystals, soluble in 5 or 6 parts of cold and 2½ of hot water. The taste of the crystals is feeble, but a concentrated solution tastes very sweet. It is insoluble in ether and alcohol. It stands between cane sugar and grape sugar in composition; for while cane sugar is $C_{12}\,H_{11}\,O_{11}$, and grape sugar $C_{12}\,H_{14}\,O_{14}$, lactine is $C_{24}\,H_{24}\,O_{24} = 2\,(C_{12}\,H_{12}\,O_{12})$. By boiling with diluted acids, it is converted into grape sugar. By the action of nitric acid, it yields *mucic* or *saccholactic acid.* It combines with ammonia and with oxide of lead. Its presence prevents the precipitation of many metallic solutions. Sugar of milk is susceptible of the vinous fermentation, and it is well known that some nations prepare an intoxicating liquor from milk by fermentation. There is reason to think that previous to fermentation, it is, like cane sugar, converted into grape sugar; and at all events milk does not ferment until an acid has been formed in it, which acid converts lactine into grape sugar.

Sugar of milk forms two compounds with oxide of lead: first, neutral, $C_{24}\,H_{19}\,O_{19}$, 5 PbO: second, basic, $C_{24}\,H_{19}\,O_{19}$, 10 PbO.

Mucic Acid, $C_{12}\,H_8\,O_{14} + 2\,HO$, is formed when diluted nitric acid acts on sugar of milk, gum, or mannite. It is a white crystalline powder, of a feebly acid taste, soluble in 6 parts of boiling water, which deposits nearly the whole on cooling. Its solution, when long heated and evaporated, yields the *modified mucic acid.* Mucic acid dissolves in oil of vitriol with a crimson colour. When heated it blackens, and yields among other products, *pyromucic acid.*

Mucic acid is bibasic, and forms two series of salts, one with 2 eq. fixed base, the other with 1 eq. fixed base, and 1 eq. water. These salts have little interest. The *mucate of oxide of ethyle* or *mucic ether*, crystallises in 4-sided prisms, soluble in hot water. When boiled with a base, it yields alcohol, and mucate of the base. Its formula is $C_{12}\,H_8\,O_{14} + 2\,AeO$.

Modified mucic acid is more soluble in water, soluble in alcohol, from which solution it is deposited in square tables. Its aqueous solution, saturated at the boiling point, deposits on cooling ordinary mucic acid. Its salts are more soluble than the mucates, but the acid in them easily passes into the ordinary acid. It is probable that the modified acid contains 1 eq. of water more than the other.

Pyromucic acid, $C_{10}\,H_3\,O_5 + HO$, is formed by the dry distillation of mucic acid. 1 eq. of mucic acid, $C_{12}\,H_{10}\,O_{16}$, contains the elements of 1 eq. pyromucic acid, $C_{10}\,H_4\,O_6$, 6 eq. water, $H_6\,O_6$; and 2 eq. carbonic acid, $C_2\,O_4$. Pyromucic acid forms brilliant white scales, fusible at 266°, and volatilises completely at a temperature somewhat higher. It is soluble in water and alcohol. Its salts are not important. *Pyromucate of oxide of ethyle*, $C_{10} H_3 O_5$, Ae O, is a solid crytallisable compound, fusible at 93°, volatile at 410°. Chlorine acts on this ether, forming a new compound, $C_{14} H_8 Cl_4 O_6$, the constitution of which is quite uncertain.

4. *Sugar of mushrooms.*—Wiggers obtained from ergot of rye a saccharine compound, crystallising in transparent rhombic prisms, soluble in water and alcohol, and susceptible of the vinous fermentation. An analysis of this sugar gave the formula $C_{12} H_{13} O_{13}$, that is, grape sugar, *minus* 1 eq. water. This may be a distinct kind of sugar ; but the mushroom sugar of Braconnot is *mannite* or manna sugar.

We have seen that starch and woody fibre may be converted into grape sugar by boiling with dilute sulphuric acid ; in like manner, salicine and phloridzine, boiled with the same acid, yield saliretine and phloretine, in each case along, with grape sugar. But the action of the infusion of malt is still more singular ; we have seen that starch by contact with infusion of malt is rapidly converted into grape sugar. This action is ascribed to the presence of *diastase*, a nitrogenised body which exists in malt, and which, while it causes the conversion of starch into sugar, itself disappears. The action is not fully understood, but there is no doubt that when seeds germinate, the starch they contain is in this manner rendered soluble, and conveyed, as sugar, to all parts of the plant, there to be converted into woody fibre by a process the inverse of that by which woody fibre is converted into sugar. This latter is seen in the ripening of fleshy fruits, where a quantity of cellular matter (lignine) disappears, and the proportion of sugar very much increases.

VINOUS OR ALCOHOLIC FERMENTATION.

This name is given to that change by which sugar is resolved into alcohol and carbonic acid, by contact with a ferment. The sugar must be dissolved in water, and the solution must be exposed to a temperature of from 40° to 86°. If a ferment, such as yeast, be added, the sugar soon disappears, carbonic acid is given off in large quantity, and the liquid is found to contain alcohol, which may be separated by distillation. Now, grape sugar, $C_{12} H_{14} O_{14}$, contains the elements of 2 eq. alcohol, 4 eq. carbonic acid, and 2 eq. water, $2 (C_4 H_6 O_2) + 4 C O_2 + 2 H O$; and, by very exact experiments it has been proved that 100 parts of grape sugar yield only 47·12 of alcohol, 44·84 of carbonic acid, together 91·96 parts, the loss, 9·04 parts being the 2 eq. of water separated. On the other hand, cane sugar, $C_{12} H_{11} O_{11}$, requires the addition of 1 eq. of water to yield 2 eq. alcohol, and 4 eq. carbonic acid, $= 2 (C_4 H_6 O_2) + 4 C O_2$; and here also experiment has demonstrated that 100 parts of cane sugar yield 53·727 parts of alcohol and 51·298 of carbonic acid, together 105·025; the increase, or 5·025 parts being due to the 1 eq. of water taken up to form dry grape sugar, $C_{12} H_{12} O_{12}$, into which cane sugar is converted before it undergoes fermentation. These facts prove that the ferment takes no direct part in the reaction, but only acts by inducing a state of change.

A considerable number of substances, if in a state of decomposition, act as ferments on a solution of sugar; among these are, besides yeast, vegetable gluten, albumen, caseine or fibrine, and the corresponding animal substances; also animal matter generally, if in a state of putrefaction.

The only explanation we can give is that the particles of these bodies, being in a state of decomposition, are in motion, and by communicating, mechanically, an impulse or motion to the particles of the sugar, destroy the balance of affinities to which the existence of sugar is owing; and thus give rise to a new balance or equilibrium, more stable under the given circumstances. The elementary particles of the sugar being disturbed in their previous arrangement, group themselves according to their individual affinities, and while the carbon forms, on one side, a compound containing all the hydrogen (alcohol), it yields on the other, a compound containing the greater part of the oxygen (carbonic acid).

When a natural juice, as that of the grape, ferments, some of the various substances it contains undergo a decomposition, probably of an analogous kind, giving rise to other new products, which are important in regard to the flavour of the liquid (wine, beer, or spirits), produced in the fermentation. Thus all wine contains œnanthic ether; potato spirit contains the oil of potato spirit (*Fuseloel.* German): grain spirit contains a similar oil. It is not improbable, that besides the vinous fermentation which takes place in the greater part of the sugar, a peculiar reaction occurs, between a portion of the sugar and the ferment (or some other nitrogenised compound present), the result of which is the production of these peculiar oily liquids. The *bouquet*, or so much prized flavour of the finer wines, is doubtless owing to some ethereal compound produced in a similar way, but the origin, properties, and composition of which are as yet altogether unknown. It may be mentioned here, however, that œnanthic ether, which is the cause of that peculiar smell which belongs to all wine, and is so marked that we can at once tell, after many weeks or months, that an empty bottle has formerly contained wine, is a compound of oxide of ethyle with a fatty acid; and the oil of potato spirit is a compound analogous to alcohol; the hydrated oxide of a radical *amyle*, $C_{10} H_{11}$.

LACTIC FERMENTATION.

When a solution of sugar is placed in contact with pressed curd, or unsalted skimmed-milk cheese, which has previously been exposed to the atmosphere for some time, and the mixture is kept at a temperature from about 75° to 90°, a peculiar change takes place, which has been called a fermentation, but which differs from the vinous fermentation in this, that the escape of gas does not appear to be essential to it. The liquid soon becomes acid, from the conversion of sugar into lactic acid; but when the amount of free acid reaches a certain point, the fermentation is thereby checked. If now the free acid be neutralised by the addition of carbonate of soda, or carbonate of lime (chalk), lactate of soda or of lime is formed, carbonic acid is disengaged, and the fermentation recommences. By repeating the addition of soda or chalk as often as free acid appears, the whole of the sugar may be at last converted into lactic acid, and obtained in the form of lactate of soda or of lime.

The best method is to dissolve 1 part of cane sugar or sugar of milk in about 5 of water, to add at the commencement $\frac{1}{2}$ part of prepared chalk, and a proper quantity of curd or cheese, and to place the whole in a temperature of 77° to 90°. Effervescence occurs, owing to the decomposition of the chalk, and in process of time the lactate of lime is deposited in small round masses of minute crystals, in such quantity as to solidify the whole mixture. This result sometimes takes place in ten days, at other times, according to the precise temperature or the state of the curd, not till after several weeks or even months. But when it is complete, which is known by the cessation of the disengagement of gas and the solidification of the mass, the sugar appears to be entirely converted into lactic acid, without the formation of any other product. This is the true lactic fermentation; but, as we shall see, it is apt to be mixed and complicated with other forms of decomposition.

The conversion of sugar, $C_{12} H_{11} O_{11}$, or of lactine, $C_{12} H_{12} O_{12}$, into lactic acid, $C_6 H_5 H_5 HO$, or $C_{12} H_{10}$

O_{10} 2 HO, is very simple; for lactine already contains the elements in the necessary proportion, and cane sugar requires only the addition of 1 eq. of water. It is therefore probable, *à priori*, that no other product should be formed along with the lactic acid; and in several of my own experiments, I have obtained so large a quantity of lactate of lime as to lead to that conclusion, while I could detect no other product, except some colouring matter and a little undecomposed sugar.

It is this fermentation which occurs in milk when exposed to the air. The caseine enters into the state in which it becomes capable of exciting the lactic fermentation in the sugar of milk (lactine); but as soon as the liquid becomes very acid, the fermentation is checked, unless an alkali be added. Hence sour milk contains both lactic acid and undecomposed lactine; but by the occasional addition of alkali the whole lactine may be converted into lactic acid, or rather, lactate of soda.

VISCOUS FERMENTATION.

When certain saccharine juices, such as those of beet-root, carrots, onions, &c., are exposed to a temperature of from 86° to 104°, a peculiar fermentation takes place. The sugar disappears, but instead of alcohol and carbonic acid, there are obtained *mannite*, *lactic acid*, and a mucilaginous substance, having the composition of gum; this latter renders the liquid ropy and viscid, hence the name given to the process.

The composition of mannite is . . .	$C_6\ H_7\ O_6$
That of lactic acid is	$C_6\ H_5\ O_5$
Together	$C_{12}\ H_{12}\ O_{11}$

It is evident, therefore, that 1 eq. of dry grape sugar, $C_{12}\ H_{12}\ O_{12}$, losing 1 eq. oxygen, might give rise to mannite and lactic acid. The gum has the same composition as sugar, so that we are led to believe that the nitrogenised constituents of the juice are acted on by the sugar, from which they obtain oxygen; and that these compounds are themselves decomposed by the oxygen, mannite, and lactic acid, which are very permanent, being produced from the sugar.

There is every reason to believe that the viscous fermentation is a mixed process, consisting of the lactic fermentation and of another, the true viscous fermentation, the products of which are gum and mannite. In the preparation of lactic acid from sugar, with the aid of curd as above described, I have sometimes obtained a little mannite, but always in so small a proportion as to indicate that its production was not essentially connected with that of the lactic acid, while in other experiments no mannite appeared. Where mannite did occur, I am inclined to suppose that the lactic fermentation was more or less complicated with the viscous.

BUTYRIC FERMENTATION.

After the sugar, in the lactic fermentation, has been converted as above described, into lactate of lime, if the mixture, still containing the caseine or curd, be kept for some time in a temperature of from 90° to 105°, the nearly solid mass of lactate dissolves by degrees, while a mixture of hydrogen and carbonic acid gases is given off, and at last the whole mass, except the cheese and any excess of chalk, becomes liquid. When the disengagement of gas has ceased, the liquid is found to contain no lactate, but only butyrate of lime; and this salt may be thus easily obtained in any quantity. The conversion of lactic into butyric acid is easily explained; for $\underbrace{2\,C_6\,H_6\,O_6}_{\text{Lactic Acid.}} = \underbrace{C_8\,H_8\,O_4}_{\text{Butyric Acid.}} + H_4 + 4\,C\,O_2$; and it is probable that no other product is formed; for in some experiments I have seen the lactate converted entirely into pure butyrate of lime, which crystallised to the last drop.

It is evident that under certain circumstances, the three kinds of fermentation just described may occur simultaneously, so that the liquid may contain lactic acid, butyric acid, mannite, gum, and unchanged sugar.

Mannite, $C_6\,H_7\,O_6$ occurs as the chief ingredient of manna. It is also found in certain juices, in mushrooms, in roots, such as that of celery, and is formed artificially as above described. It is easily purified by solution in alcohol and crystallisation. It forms, when crystallised in water, large prisms, of a weak sweet taste. It is not susceptible of the vinous fermentation. Nitric acid and permaganate of potash act on it as on sugar. Concentrated arsenic acid gives it a brick red colour.

Lactic Acid, $C_6\,H_5\,O_5 + H\,O$, so called because it occurs in sour milk, is also formed abundantly, as above described, in a peculiar fermentation of certain saccharine juices at a high temperature. In milk it is derived from the sugar of milk; and by neutralising sour milk with carbonate of soda, adding sugar of milk, allowing it again to become acid, again neutralising, and so on in succession, as long as the caseine causes the peculiar change to take place, it may be obtained in large quantity. A still easier process is to dissolve 14 parts of cane sugar in 60 of water, and to add 4 of moist cheese and 7 of prepared chalk. The mixture being kept some time at from 77° to 86° F. will at last become quite thick with crystals of lactate of lime. If the action of the caseous ferment be pushed further, and at a higher temperature, the lactate of lime is not obtained, but in its place, *butyrate of lime* in large quantity. See *Butyric Fermentation.* The above quantities will yield about 13 parts of lactate after it has been purified by crystallisation; besides from 1½ to 2 parts of mannite. The acid of sour crout is lactic acid, and by boiling the juice of sour crout with chalk or carbonate of zinc, lactate of zinc or of lime may be obtained.

Liebig has lately shown that lactic acid exists abundantly in the juice of flesh; and as abundantly in the flesh of carnivorous as in that of herbivorous animals. This is remarkable, as the food of carnivorous animals contains no saccharine or amylaceous matter, so that the lactic acid must be formed from albuminous compounds. The same remark applies to the occurrence of lactine in the milk of carnivora.

It has been stated by Cap and Henry, that lactic acid exists in normal urine, as lactate of urea; but I have never been able by their process to obtain from urine a trace of lactic acid, nor anything but pure urea. Pelouze and others were equally unsuccessful; and Liebig has proved by experiments on a very large scale, that urine contains no lactic acid in the normal state; and further, that lactic acid, taken internally, cannot be recognised in the urine.

From the lactate of lime, lactic acid may be obtained by the action of oxalic acid, which removes the lime as oxalate. The filtered solution is lactic acid, which is concentrated by evaporation, and purified by solution in ether. From the lactate of soda, lactate of zinc may be obtained by adding chloride of zinc to the hot saturated solution; on cooling, lactate of zinc, being sparingly soluble in cold water, crystallises. This salt, acted on by barytic water, yields lactate of baryta, from which sulphuric acid removes the baryta, and the filtered liquid is pure diluted lactic acid.

In its most concentrated form, hydrated lactic acid is a syrupy liquid, of a very strong but pleasant acid taste. Its Sp. G. is 1·215. Its formula $C_6 H_5 O_5 + HO = C_6 H_6 O_6$; but according to Engelhardt and Maddrell it is bibasic, $C_{12} H_{10} O_{10}, 2 HO = C_{12} H_{12} O_{12}$. It is therefore polymeric with dry grape sugar and with gum; both of which are $C_{12} H_{12} O_{12}$. At 482° the hydrate is decomposed, and yields a solid crystalline sublimate, $C_6 H_4 O_4$, which has been called anhydrous lactic acid, or sublimed lactic acid. This compound dissolves readily in hot water, and the solution if evaporated yields the original hydrate $C_6 H_6 O_6 = C_6 H_4 O_4 + 2 HO$. But when the acid is neutralised by bases, only one of the 2 eq. of water taken up by the sublimed acid is replaced by a base; and consequently we cannot look on the sublimed acid as the true anhydrous acid. The anhydrous acid, as it exists in the lactates, is $C_6 H_5 O_5$; and the sublimed acid is not lactic acid, but is converted into lactic acid when boiled with water.

The general formula for the lactates is $C_6 H_5 O_5, MO$; or $C_{12} H_{10} O_{10}\ 2HO$. The lactates of the alkalies are very soluble and deliquescent: that of lime is less soluble in cold water and crystallises readily. The lactate of zinc is sparingly soluble in cold water, and is hence well adapted for the extraction and purification of the acid.

XIX. Methyle. $C_2 H_3 = Mt$.

This is the hypothetical radical of a numerous series of compounds, entirely analogous to those of ethyle. There is the *oxide of methyle*, $Mt O$, analogous to oxide of ethyle; and the *hydrated oxide of methyle*, $Mt O, H O$, analogous to alcohol. This last is the compound from which all the others are obtained. The extraordinary analogy between ethyle and methyle will enable us to describe the compounds of the latter very briefly.

1. Hydrated Oxide of Methyle. $Mt O, H O$.

Syn. *Pyroxilic Spirit*. This compound is one of the chief products of the destructive distillation of wood, and is found in the watery portion along with acetic acid, acetone, acetate of oxide of methyle, and several other ethereal liquids, besides portions of the oily matter of the tar dissolved in them.

By rectification with chloride of calcium, the pyroxilic spirit, which combines with that salt, is separated from several other liquids which distil over in the heat of the vapour bath. The residue, if mixed with its own bulk of water, and again heated in the vapour bath, now gives off the pyroxilic spirit, which is still mixed with water. It is purified by rectification with quicklime, which also destroys any acetate of methyle that may be present.

Pure hydrated oxide of methyle is a liquid very similar to alcohol, having the same density, and the same degree of inflammability. Its odour is peculiar and ethereal. It boils at about 140° or 150°.

When heated with peroxide of manganese, water, and sulphuric acid, it yields various products, among which the chief are, *formic acid* and *formomethylal.* It is decomposed by nitric acid, yielding oxalic acid, and by chlorine, yielding new products. It dissolves resins, and is used in making varnishes. It forms with baryta a crystalline compound $BaO + MtO, HO$; and, with chloride of calcium, another crystalline body in large hexagonal tables, $CaCl + 2\,(MtO, HO)$.

By the action of platinum powder, pyroxilic spirit is oxidised into formic acid, which bears the same relation to it that acetic acid does to alcohol.

2. Oxide of Methyle. $Mt\,O = (C_2\,H_3)\,O$.

This compound is obtained, like ether (oxide of ethyle) when the preceding compound is distilled with its own volume of oil of vitriol; it escapes as an inflammable gas. Like oxide of ethyle, it is a base and neutralises acids. It even forms a neutral sulphate, which oxide of ethyle cannot do. It is worthy of notice, that oxide of methyle is polymeric with alcohol; for $C_4\,H_6\,O_2 = 2\,(C_2\,H_3\,O)$: so that these two bodies have the same composition, in 100 parts; that is, the same relative proportions of the same elements, but a very different absolute amount: the equivalent of alcohol being twice as heavy as that of oxide of methyle. The constitution of these compounds, moreover, is different, for one is a hydrate, $C_4\,H_5\,O + HO$; while the ether is an anhydrous oxide, $C_2\,H_3\,O$.

3. *Chloride of methyle*, $C_2\,H_3, Cl = Mt\,Cl$, is a gas, of an ethereal smell, inflammable, of Sp. G. 1·1737. It is formed by the action of sulphuric acid and chloride of sodium on pyroxilic spirit. By the action of chlorine, aided by the sun's rays, it yields several new compounds containing chlorine.

4. *Iodide of methyle*, $C_2\,H_3, I = Mt\,I$, is obtained by distilling 12 parts of pyroxilic spirit, 8 of iodine, and 1 of phosphorus. It is a liquid boiling between 102° and 122°. The *fluoride* and *cyanide* of meythle are analogous liquids.

5. *Sulphuret of methyle*, $C_2\,H_3, S = MtS$, is best formed by the action of a current of chloride of methyle on sulphuret of potassium dissolved in alcohol. $MtCl + KS = MtS + KCl$. It is a mobile liquid, of a very offensive alliaceous odour, boiling at 104°. Its Sp. G. in the liquid form is 0·845; in the form of vapour, it is 2·115. With chlorine, it gives rise to several new compounds. The *hydrosulphuret* of *sulphuret of methyle* (corresponding to mercaptan) l obtained by distilling the double sulphate of methyle and potash with the hydrosulphuret of sulphuret of potassium. $(KO, MtO, 2SO_3) + HS, KS = 2\,(KO, SO_3) + HS, MtS$. Its formula is HS, MtS

$= C_2 H_3, S + HS$. It is a colourless liquid, lighter than water, which boils at 70°, and acts on the oxides of mercury and lead exactly as mercaptan does. It odour is most offensive, resembling that of leeks highly concentrated.

SALTS OF OXIDE OF METHYLE.

1. *Neutral Sulphate.* MtO, SO_3, is obtained when pyroxilic spirit is distilled with a large excess of sulphuric acid. It forms an oily liquid, of a slightly alliaceous smell. It boils at 370°. Boiling water decomposes it into acid sulphate and hydrate of oxide of methyle. When heated with chlorides, cyanides, &c., it yields the compound of methyle with chlorine, cyanogen, &c.; with a salt of benzoic, succinic, or other organic acid, it yields benzoate, &c. of oxide of methyle. Ammonia converts it into *sulphamethylane.*

2. *Bisulphate of Oxide of Methyle.* SYN. *Sulphomethylic Acid.* $HO, MtO, 2 SO_3$, is perfectly analogous to sulphovinic acid, and forms double salts, such as that of potash, $KO, MtO, 2 SO_3$, which are often called sulphomethylates, and correspond exactly to the sulphovinates. The acid sulphate itself may be obtained in crystals, which are very soluble and very acid. It is best obtained by the action of hot water on the neutral sulphates. The double salts, or sulphomethylates, are of no particular importance. They crystallise readily.

3. *Nitrate of Oxide of Methyle,* MtO, NO_5, is obtained when pyroxilic spirit is distilled with nitrate of potash and sulphuric acid. It is an oily liquid, the vapour of which if heated beyond 248° explodes violently.

The neutral carbonate of methyle is not known; but double carbonates, analogous to those of ethyle with alkalies, may be prepared in the same way as those compounds.

4. *Oxalate of Oxide of Methyle,* $MtO, C_2 O_3 = C_4 H_3 O_4$, is obtained in a manner analogous to that in which oxalic ether is prepared. It forms a crystalline solid, soluble in alcohol and pyroxilic spirit, which deposit it in large crystals. By the action of dry ammonia, it is converted into *oxamethylane* (analogous to oxamethane), which is the *oxamate of oxide of methyle,* $C_6 H_5 NO_6 = C_2 H_3, O + C_4 H_2 NO_5$. Liquid ammonia converts it into oxamide, as is the case with oxalic ether, only here pyroxilic spirit and not alcohol is formed at the same time. $C_2 H_3, O, C_2 O_3 + NH_3 = C_2 H_3 O, HO + C_2 O_2 NH_2$. This is perhaps the easiest way of obtaining oxamide in large quantity.

Bisulphuret of carbon and hydrated cyanic acid act on pyroxilic spirit exactly as on alcohol, producing analogous compounds.

5. *Benzoate of Oxide of Methyle*, $Mt O, Bz O$, is best obtained by distilling dry benzoate of lime or soda with neutral sulphate of methule. It is an oily liquid of a balsamic odour, analogous in other respects to benzoic ether.

6. *Acetate of Oxide of Methyle*, $Mt O, Ac O_3$, is obtained in the same way as acetic ether, which it resembles. It occurs in considerable quantity in raw pyroxilic spirit, and even in that which has only been purified by rectification. When quicklime is used in the rectification, it is destroyed, yielding an additional quantity of the pure hydrate of oxide of methyle. It is very volatile and inflammable, and for most purposes its presence in the wood spirit is not at all injurious. It is isomeric with formiate of oxide of ethyle: for $C_2 H_3 O + C_4 H_3 O_3 = C_4 H_5 O + C_2 H O_3$.

7. *Salicylate of Oxide of Methyle* exists ready formed, as the volatile oil of *Gaultheria procumbens*, or *Wintergreen*. It is very fragrant, and plays the part of an acid, combining with alkalies. When heated with them, however, salicylates are formed, and pyroxilic spirit set free. It is a very interesting compound, as it contains two substances previously only known as artificial products; namely, salicylic acid and oxide of methyle. It is acted on by nitric acid and other re-agents exactly in the same way as the salicylate of oxide of ethyle, which see.

The mucate of oxide of methyle is a crystalline solid, analogous in its preparation and properties to the corresponding salt of ethyle.

The action of chlorocarbonic acid on pyroxilic spirit is exactly analogous to its action on alcohol, producing an oily liquid, $C_4 H_3 Cl O_4 = C_2 \left\{ \begin{matrix} O_3 \\ Cl \end{matrix} \right. + C_2 H_3 O$. By the action of ammonia, this liquid produces a compound, *urethylane*, (corresponding to *urethane*) $C_4 H_5 N O_4$ or $C_8 H_{10} N_2 O_8 = C_2 H_4 N_2 O_2 + 2 (C_2 H_3 O, CO_2)$; that is, a compound, possibly, of 1 eq. urea, with 2 eq. neutral carbonate of methyle, but more probably of carbamic acid, CO_2, $CONH_2$, and oxide of methyle, $C_2 H_3 O$.

When a current of ammonia is made to act on the neutral sulphate of methyle, there is produced a crystalline compound, $C_2 H_5 N S_2 O_6$, which has been called *sulphamethylane*, and may be viewed as oxamethylane, in which sulphamide, SO_2, NH_2, has been substituted for oxamide, $C_2 O_2 NH_2$; or SO_2 for $C_2 O_2$. It may also be considered, if oxamethylane be the oxamate of oxide of methyle, $C_2 H_3 O + C_4 H_2 NO_5$, as composed of oxide of methyle and a peculiar acid, formed of hyposulphuric acid and amide, or rather of sulphuric acid and sulphamide, and which may be called *sulphamic acid;* and its formula will be $C_2 H_3 O + (S_2 O_5, NH_2)$, or $C_2 H_3O + (SO_3 + NH_2, SO_2)$. On this view, sulphamethylane is the sulphamate of oxide of methyle.

When hydrated oxide of methyle is oxidised by means of platinum powder, it is finally converted into pure formic acid. There is evidently, therefore, the same relation between methyle and formic acid, as between ethyle and acetic acid; and on comparing the formulæ of pyroxilic spirit and of formic acid, $C_2 H_3 O, HO$, and $C_2 HO_3, HO$, we perceive that the former, to be converted into the latter, must have lost 2 eq. of hydrogen, and taken up 2 eq. of oxygen. This is exactly what takes place with alcohol, and there can be no doubt, that the pyroxilic spirit yields an intermediate compound, exactly analogous to aldehyde, although this has not yet been isolated. Such a compound would be the hydrated protoxide of a derived radical, *formyle*, analogous to acetyle, of which formic acid is the hydrated peroxide; and its formula would be $(C_2 H) O + HO$. We shall, therefore, assume the existence of this radical, and proceed to describe its compounds, which are quite analogous to those of acetyle.

XX. Formyle. $C_2 H = Fo$.

This radical is unknown in a separate form, as are its protoxide and deutoxide, corresponding to aldehyde and aldehydic acid. But when hydrated oxide of methyle is distilled with sulphuric acid, water, and peroxide of manganese, a volatile liquid is obtained, which is a mixture of formiate of oxide of methyle, and another liquid called methylal. When purified, this latter has the formula $C_6 H_8 O_4$, which indicates, that it is composed of $C_2 HO, HO$, or hydrated oxide of formyle, and 2 eq. of oxide of methyle, $2 (C_2 H_3 O)$. This compound, briefly, $FoO, HO + 2 MtO$, corresponds to acetal in the series of ethyle; acetal being $AcO, HO + AeO$.

Formic Acid. $C_2 HO_3, HO = FoO_3 HO$.

This remarkable acid occurs in the red ant, *formica rufa*, and may be obtained, in a diluted and impure state, by infusing these insects in water. Its production from pyroxilic spirit has been described above. It may also be prepared by distilling a mixture of starch or sugar with peroxide of manganese, water, and sulphuric acid; and it is formed under a great variety of circumstances from many organic compounds.

To prepare the hydrated acid pure and concentrated, the dry formiate of lead, PbO, FoO_3, is decomposed by sulphuretted hydrogen gas, and the vapour of the formic acid condensed in a well-cooled receiver. It is boiled for a few moments to expel any sulphuretted hydrogen. It is a clear liquid of Sp. G. 1·235, fuming slightly, and has a very pungent acid smell. Below 32° it crystallises in brilliant scales. It boils at 212°, and its vapour is inflammable, burning with a blue flame. This is probably owing to the formation of carbonic oxide, for the acid $C_2\ HO_3$, HO, contains the elements of 2 eq. carbonic oxide, $C_2\ O_2$, and 2 eq. water, $H_2\ O_2$.

With 1 eq. of water it forms the second hydrate $FoO_3 + 2\ HO$, which much resembles the first in properties. Its boiling point is 221°, and its Sp. G. is 1·110.

Both these hydrates are highly corrosive; a drop of either on any delicate portion of the skin causes a severe burn, which blisters, suppurates, and is very painful and difficult to heal. In this respect, the formic acid can only be compared to hydrofluoric and hydrated cyanic acids.

A weaker acid is obtained by distilling formiate of soda, lime, or lead, with sulphuric acid, previously diluted with half its weight of water. Ten parts of formiate of lime, 8 of oil of vitriol, and 4 of water, yield 9 of formic acid, of Sp. G. 1·075.

The salts of the acid are best prepared from the weak and impure acid obtained by distilling a mixture of 10 parts of starch, 37 of peroxide of manganese, 30 of oil of vitriol, and 30 of water. These materials yield 3·35 parts of formic acid, such that 100 parts neutralise 15 of dry carbonate of soda. From this acid, the formiate of lead may be easily prepared and purified; and from it, by the addition of carbonate of soda, formiate of soda may be obtained.

Formic acid is easily recognised by the action of sulphuric acid, which decomposes, without blackening, both it and its salts, causing the disengagement of pure carbonic oxide. It also reduces the oxides of all the noble metals, and is itself oxidised into carbonic acid. Formic acid not only reduces the oxides, but also, in most cases, the soluble salts, of the noble metals. 1 eq. formic acid can reduce 2 eq. of a protoxide, such as that of silver, $2\ AgO + C_2\ HO_3 = Ag_2 + HO + 2\ CO_2$; or 1 eq. of a deutoxide, such as that of mercury; $HgO_2 + C_2\ HO_3 = Hg + HO + 2\ CO_2$.

Formic acid is a very powerful acid, and forms salts with bases, all of which are soluble. They are generally similar to the acetates; but yet quite distinct. Many metallic formiates, when heated in close vessels, give off carbonic acid and carbonic oxide, leaving the metal reduced: others give off carbonic oxide, leaving the oxide.

Formiate of ammonia, NH_4O, C_2HO_3, contains the elements of hydrocyanic acid and water, $C_2NH + 4HO$; and is converted into these compounds when its vapour is passed through a red-hot tube. *Formiate of oxide of ethyle*, prepared like the acetate, is a volatile ethereal liquid, with a peculiar aromatic smell. The corresponding salt of oxide of methyle is quite analogous. *Formiate of potash* is very deliquescent. *Formiate of soda* is also very soluble, but may be obtained in crystals. It is a very powerful reducing agent, both in a moist and dry way. In the former, it reduces the noble metals, in the latter, at a red heat, by virtue of the carbonic oxide it gives off, it reduces most of the reducible metals, such as lead, copper, antimony, arsenic, cobalt, nickel, &c. *Formiate of lead* is sparingly soluble in cold water, and is therefore easily purified, and serves to prepare formic acid and formiate of soda. *Formiate of deutoxide of mercury* and *formiate of protoxide of mercury* both exist. When red oxide of mercury is dissolved in cold formic acid, the former salt is produced; but the slightest heat causes an effervescence, while formiate of the protoxide is deposited in silvery scales like the acetate. These, when warmed, are decomposed with effervescence and deposition of metallic mercury. *Formiate of silver* resembles the acetate; but is very easily decomposed by heat, the metal being reduced.

COMPOUNDS OF FORMYLE WITH CHLORINE, ETC.

When chlorine or hypochlorites act on oxide of methyle, hydrated oxide of methyle, and chloride of methyle, a great variety of new compounds are produced, corresponding in most cases to the compounds obtained by the action of chlorine, &c., on alcohol, ether, and chloride of ethyle. Our space forbids us to give the details of these decompositions; but we may mention that two of the compounds formed by the action of chlorine on the compounds of ethyle and acetyle, may be viewed as *protochloride* and *bichloride of formyle*. These are $C_4H_2Cl_2 = 2(C_2H, Cl)$; and $C_4H_2Cl_4 = 2(C_2H, Cl_2)$. The *perchloride of formyle*, $FoCl_3 = C_2H, Cl_3$, is also produced from a compound of the ethyle series, namely from chloral, by the action of alkalies. It is an oily liquid of a sweet taste and ethereal smell. When acted on by alkalies, it yields chlorides and formiates; thus, with potash, $C_2HCl_3 + 4KO = 3KCl + KO, C_2HO_3$.

When acted on by chlorine, perchloride of formyle yields perchloride of carbon $C_2Cl_4 = C_2Cl, Cl_3$, just as perchloride of acetyle, $C_4 H_3, Cl_3$ yields sesquichloride of carbon $C_4 Cl_6 = C_4 Cl_3, Cl_3$.

Perbromide of formyle is obtained from bromal. *Periodide of formyle*, obtained by the action of alcohol on iodine and potash, is a yellow crystalline, volatile solid, having an odour analogous to that of saffron.

When chlorine acts on oxide of methyle, $C_2 H_3 O$, it produces, by substitution of chlorine for hydrogen, the compounds $C_2 \left\{\begin{matrix}H_2\\ Cl\end{matrix}\right. O$; $C_2 \left\{\begin{matrix}H\\ Cl_2\end{matrix}\right. O$; and finally, $C_2 Cl_3, O$. The second may be considered as formic acid, $C_2 H O_3$, in which two-thirds of the oxygen are replaced by chlorine, $C\ H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$. It will then be an *oxychloride of formyle*, analogous to oxychloride of acetyle.

When chlorine acts on chloride of methyle, $C_2 H_3 Cl$, three compounds are formed by substitution. These are, 1st, $C_2 H_2 Cl_2 = C_2 \left\{\begin{matrix}H_2\\ Cl\end{matrix}\right., Cl$; 2nd, *perchloride of formyle*, $C_2 H Cl_3 = C_2 \left\{\begin{matrix}H\\ Cl_2\end{matrix}\right., Cl$; and 3rd, as before explained, perchloride of carbon, $C_2 Cl_4 = C_2 Cl_3, Cl$.

The action of chlorine on sulphuret of methyle, $C_2 H_3, S$, appears to yield, $C_2 \left\{\begin{matrix}H_2\\ Cl\end{matrix}\right. S$; $C_2 \left\{\begin{matrix}H\\ Cl_2\end{matrix}\right. S$; and $C_2 Cl_3 S$.

The action of chlorine on oxalate, benzoate, and acetate of oxide of methyle is quite analogous to its action on the corresponding compounds of ethyle, producing the oxalate, benzoate, and acetate of oxychloride of formyle $C_2 O_3 + C_2 H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$; $C_{14} H_5 O_3, + C_2 H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$; and $C_4 H_3 O_3 + C_2 H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$. These curious results, like those which precede them, are here merely indicated, as we have explained the principle of their formation under the heads of ethyle and acetyle.

In some specimens of raw pyroxilic spirit there occurs a large proportion of a peculiar volatile liquid, which has been called *lignone* or *xylite*. As its constitution is quite uncertain, although it is believed to contain some compound of oxide of methyle, we shall state what is known of it when treating of the products of the dry distillation of wood.

XXI. CETYLE. $C_{32} H_{33} = Ct.$

This is the hypothetical radical of a series of compounds, derived from spermaceti. The principal one is *ethal*, the hydrated oxide of cetyle, analogous to alcohol.

Hydrated Oxide of Cetyle. $C_{32} H_{33} O, H O = Ct O, H O$.

Syn. *Ethal.* This compound exists in spermaceti, in combination with cetylic or ethalic acid $C_{32} H_{31} O_3$. When spermaceti is digested with strong caustic potash, a soap is produced; and this being decomposed by sulphuric acid, yields a fatty mixture composed of cetylic acid and ethal. The whole is acted on by baryta, with which the acids unite; and the ethal is dissolved from the mixture by cold alcohol. It is afterwards purified by means of ether.

Ethal forms a white crystalline solid, like wax, fusible about 118°, volatile at a higher temperature, soluble in alcohol. As above mentioned, it is analogous to alcohol; and although the oxide of cetyle has not yet been obtained in a separate form, yet there have been formed the *chloride of cetyle*, and the *double sulphate of oxide of cetyle and potash*, analogous to the corresponding compounds of ethyle.

When ethal is repeatedly distilled with anhydrous phosphoric acid, it loses the elements of 2 eq. of water, yielding a new compound, cetene$=C_{32} H_{32}$, analogous to olefiant gas or etherine. It is an oily inflammable liquid. *Cetylic* or *ethalic acid* will be hereafter described. Its formula is $C_{32} H_{31}, O_3, H O = C_{32} H_{32} O_4$; it belongs to the series $(C H) n + O_4$.

XXII. AMYLE. $C_{10} H_{11} = Ayl$.

This is the hypothetical radical of a series of compounds, derived from oil of potato spirit, which is itself, when pure, the hydrated oxide of amyle, analogous to alcohol. Both the radical and its anhydrous oxide are unknown in the separate state; but a sufficient number of compounds has been obtained to render its existence highly probable.

Hydrated Oxide of Amyle. $C_{10} H_{11} O, H O = Ayl O, H O$.

Syn. *Oil of potato spirit*; in German *Fuscloel.* This compound distils over towards the end of the first distillation of spirits made from potatoes, rendering these last portions of the spirit milky and very offensive. It separates on standing as an oily liquid, which is washed with water to remove alcohol, dried by chloride of calcium, and rectified till its boiling point becomes steady at 269° or 270°. It is then pure.

It is a colourless oily liquid, very mobile, of a strong and nauseous odour, which produces stupifying effects. Its vapour, when inhaled, causes cough and spasmodic dyspnœa, resembling asthma, often followed by vomiting. Its taste is very acrid and nauseous. Its Sp. G. is 0·812. At — 4° it crystallises in shining scales. When heated with dry hydrate of potash it is oxidised, hydrogen being given off, and the potash is found combined with valerianic acid, $C_{10}\,H_9\,O_3$. When distilled with anhydrous phosphoric acid, it yields a new carbohydrogen, *amilene* $= C_{10}\,H_{10}$.

The *chloride of amyle* has not yet been obtained; but the *bromide* and *iodide* are formed when the hydrated oxide is distilled along with phosphorus and bromine or iodine. They are both heavy oily liquids, and their formulæ are Ayl Br. and Ayl I.

The *bisulphate of oxide of amyle* or *sulphamilic acid*, Ayl O, H O, 2 $S\,O_3$, is analogous to sulphovinic acid. With bases, it forms double salts, the formula of which is M O, Ayl O, 2 $S\,O_3$, which are soluble in water and crystallisable. The solutions, when boiled, yield hydrated oxide of amyle, free sulphuric acid, and a neutral sulphate.

The *acetate of oxide of amyle* is an ethereal liquid, analogous to acetic ether. Its formula is $C_{14}\,H_{14}\,O_4 = C_{10}\,H_{11}\,O, C_4\,H_3\,O_3$ = Ayl O, Ac O_3.

The *hydrosulphuret of sulphuret of amyle*, Ayl S, H S, is prepared in the same way as mercaptan, to which it is quite analogous. It is an oily liquid boiling at 243°, of Sp. G. 0·835. It has, like the corresponding compounds of ethyle and methyle, a most penetrating odour of onions; and, like them, it acts on red oxide of mercury, forming a white crystalline compound Ayl S, Hg S.

The *sulphocarbonate of oxide of amyle*, very analogous to the bisulphocarbonate of oxide of ethyle, is formed when bisulphuret of carbon acts on a solution of potash in oil of potato spirit.

OXIDATION OF HYDRATED OXIDE OF AMYLE.

Valerianic Acid. $C_{10}\,H_9\,O_3, H\,O = C_{10}\,H_{10}\,O_4$.

It has already been mentioned, that when oil of potato spirit is heated with dry hydrate of potash, hydrogen is given off, and valerianate of potash is formed. Here the oil, $C_{10}\,H_{11}\,O$, H O, loses 2 eq. hydrogen, and gains 2 eq. oxygen; so that valerianic acid stands to amyle in the same relation as acetic acid to ethyle, and formic acid to methyle. The acid is easily separated by distilling the salt of potash with diluted sulphuric acid. In composition and in all its properties, it agrees with the native valerianic acid, obtained by distilling the root of *valeriana officinalis* with water. It belongs to the series of acids, the general formula of which is $(C\,H)\,n + O_4$.

Valerianic acid is a limpid, oily fluid, of a disagreeable and peculiar smell. Its. Sp. G. is 0·944, and it boils at 270°. With bases, it forms soluble salts, which have a sweet taste.

The action of chlorine on hydrated oxide of amyle gives rise to the formation of a compound, *chloramilal*, supposed to be analogous to chloral, but the composition and nature of which are not fully known.

Amilene, the carbo-hydrogen obtained by distilling hydrated oxide of amyle with dry phosphoric acid, has the formula $C_{10}\,H_{10}$, and is, like cetene, isomeric with olefiant gas.

XXIII. Glyceryle. $C_6\,H_7 = Gl.$

This is the hypothetical radical of glycerine, a basic compound which exists in all neutral fat oils combined with oily acids.

Hydrated Oxide of Glyceryle. $C_6\,H_7\,O_5 + H\,O = Gl\,O_5\,H\,O.$

Syn. *Glycerine.* To obtain it, olive oil is converted into plaster by long boiling with litharge and water. When the plaster is completely formed, the glycerine is found dissolved in the water. It is purified from lead by sulphuretted hydrogen, and is then concentrated in the vapour bath and finally in vacuo. When pure, it forms a viscid syrup, colourless or slightly yellow. It has a decided sweet taste, and its Sp. G. is 1·252. By the action of heat it is decomposed, yielding a peculiar volatile compound, *acroleine*, which attacks the eyes most powerfully. This substance has lately been studied by Redtenbacher: we shall give his results when treating of the action of heat on fat oils.

With sulphuric acid, glycerine forms an acid sulphate $C_6\,H_7\,O_5,\,H\,O,\,2\,S\,O_3$; which forms double salts, analogous to the sulphovinates, the formula of which is, $MO,\,Gl\,O_5,\,2\,S\,O_3$.

There is reason to believe that the basic compound in oils has not the composition of the isolated glycerine. In some oils it would appear to be $C_3\,H_2\,O$, which Berzelius calls *oxide of lipyle;* and $C_6\,H_7\,O_5 = 2\,(C_3\,H_2\,O) + 3\,H\,O$. On this view, oxide of lipyle, when separated, combines with water to yield glycerine. We shall also see that acroleine, the product of the action of heat on glycerine is $C_6\,H_4\,O_2 = 2\,(C_3\,H_2\,O.)$

Having now briefly described the known or admitted organic radicals and their derivatives, we proceed to consider the organic acids whose composition is known, although we cannot speak with certainty of their constitution, their radicals being yet unknown.

ORGANIC ACIDS.

1. Citric Acid. $C_{12}H_5O_{11}, 3HO = \overline{Ci}, 3HO$.

This acid is found in many vegetable juices, especially those of sour fruits, as the lemon, lime, orange, red currant, &c. It is extracted by adding chalk to the acid juice, by which means an insoluble citrate of lime is formed. This is decomposed by diluted sulphuric acid with the aid of heat, and the solution, filtered from the sulphate of lime, gives on evaporation and cooling crystals of citric acid, consisting of $\overline{Ci}, 3HO + aq$. A slight excess of sulphuric acid promotes the crystallisation.

It forms large transparent crystals, very soluble in water, of a very strong and agreeable acid taste. A diluted solution is soon decomposed, becoming mouldy. By spontaneous evaporation of a saturated solution, crystals may be obtained, which are $\overline{Ci}, 3HO + 2aq$. At 212°, these lose the 2 eq. of water of crystallisation. The other crystals, above mentioned, do not lose water at 212°, but melt at 256°; and when heated beyond 300°, both kinds are decomposed. Heated with oil of vitriol in excess, citric acid is decomposed, yielding,

From 1 eq. citric acid	C_{12}	H_8	O_{14}
2 eq. carbonic acid	C_2		O_4
2 eq. carbonic oxide	C_2		O_2
2 eq. acetic acid	C_8	H_6	O_6
2 eq. water		H_2	O_2
	C_{12}	H_8	O_{14}

In like manner, when fused with caustic potash, citric acid is resolved into 2 eq. of acetic acid, 2 eq. oxalic acid, and 2 eq. water.

When citric acid is added to lime-water, the liquid remains clear, but when heated becomes turbid, and deposits citrate of lime. This character serves to distinguish citric acid from most other vegetable acids.

SALTS OF CITRIC ACID.

Citric acid is tribasic, and forms three series of neutral salts, that is, of salts with 3 eq. of base, whether fixed base or basic water. It also forms basic salts, of the formula $\overline{Ci}, 3MO + MO$ or $\overline{Ci}, 3MO + MO + aq$. These basic salts correspond in constitution to the two forms of crystallised acid.

When a dry citrate, with 3 eq. of fixed base, is decomposed by an alcoholic solution of hydrochloric acid, so that no more water is presented to the citric acid than the 3 eq. of basic water derived from the hydrogen of the hydrochloric acid and the oxygen of the base, there are formed, from 3 eq. dry citric acid, 2 eq. of the acid with 1 eq. of water of crystallisation, and 3 eq. of the hydrated aconitic acid. $3\,(C_{12}\,H_5\,O_{11},\ 3\,HO) = 2\,(C_{12}\,H_5\,O_{11},\ 3\,HO + aq.) + 3\,(C_4\,HO_3,\ HO)$. This is the same change which takes place in citric acid when heated to a certain point, water being given off.

Citrate of Oxide of Ethyle, $\overline{Ci}, 3\,Ae\,O$, is an oily liquid of Sp. G. 1·142. By alkalies it is converted into citrates and alcohol.

Citrate of Potash occurs in three forms. $\overline{Ci}, 3\,KO$; $\overline{Ci}\left\{\begin{matrix}2\,KO\\ HO\end{matrix}\right.$ and $\overline{Ci}\left\{\begin{matrix}KO\\ 2\,HO\end{matrix}\right.$. All are very soluble and crystallise with difficulty.

Citrate of Soda also forms three salts. 1. $\overline{Ci}, 3\,Na\,O + 11$ aq. This salt forms large regular crystals. 2. $\overline{Ci}, 2\,Na\,O, HO$; formed by adding to a solution of the preceding salt half as much citric as it already contains. It forms, by evaporation, needles of a very pleasant subacid taste. 3. $\overline{Ci}, Na\,O, 2\,HO$. Formed by adding to a solution of No. 1, as much citric acid as it already contains. This salt does not crystallise in water, but forms a gummy mass. A saturated alcoholic solution, however, deposits crystalline grains. *Citrate of baryta* forms two varieties. 1. $\overline{Ci}, 3\,Ba\,O + 7$ aq. which falls when citrate of soda is added to chloride of barium. 2. $2\,\overline{Ci}\left\{\begin{matrix}5\,Ba\,O\\ HO\end{matrix}\right. + 7$ aq. $= \overline{Ci}\left\{\begin{matrix}2\,Ba\,O\\ H\,O\end{matrix}\right. + \overline{Ci}, 3\,Ba\,O + 7$ aq. This is deposited on cooling, when a boiling solution of citrate of soda is added to a boiling solution of chloride of barium and free citric acid. *Citrate of lime* also yields two salts. 1, neutral, $\overline{Ci}, 3\,Ca\,O + 4$ aq. formed by mixing chloride of calcium and citrate of soda. It is insoluble. 2, basic: $\overline{Ci}, 3\,Ca\,O + Ca\,O +$ aq. formed when citric acid is heated with excess of lime-water. The citrate of lime formed from lemon, or currant-juice, by chalk, is an impure mixture of the basic and neutral salts. *Citrates of lead*, 1. $\overline{Ci}, 3\,Pb\,O +$ aq. 2. $\overline{Ci}, 2\,Pb\,O, HO + 2$ aq.: 3, basic: $\overline{Ci}, 3\,Pb\,O + 3\,Pb\,O$.: 4, also basic. $\overline{Ci}, 3\,Pb\,O + Pb\,O +$ aq. These are all sparingly soluble or insoluble, and are decomposed by washing. *Citrate of copper* is basic, $\overline{Ci}, 3\,Cu\,O + Cu\,O$. *Citrate of silver* is a brilliant white, insoluble powder, $\overline{Ci}, 3\,Ag\,O +$ aq. It loses its water under 80°. *Citrate of antimony and potash* is a double salt, $\overline{Ci}, Sb_2O_3 + \overline{Ci}, 3KO + 5aq.$ It forms hard, brilliant, white prisms, which lose their water at 212°.

ACTION OF HEAT ON CITRIC ACID.

The first effect of heat on crystallised citric acid is to melt it, and the next, to expel the water of crystallisation. The acid, if now dissolved, crystallises unchanged. But if the heat be continued, there is given off gas and inflammable vapours, and the residue is no longer citric acid but hydrated aconitic acid.

1 eq. crystallised citric acid	$C_{12}H_5O_{11}+3HO+2aq.$
Yields, first,—5 eq. of water . . .	$3HO+2aq.$
then— 1 eq. aconitic acid (hydrated)	$C_4H_2O_4$
4 eq. carbonic oxide . .	C_4O_4
1 eq. acetone . . .	$C_3H_3O_1$
1 eq. carbonic acid . .	C_1O_2
	$C_{12}H_5O_{11}+3HO+2aq.$

When the heat is increased, other products appear, particularly two new acids: but these are derived from aconitic acid. They are *itaconic* and *citraconic acids.*

Aconitic Acid. $C_4HO_3, HO = \overline{At}.$

SYN. *Equisctic Acid.*—This acid occurs native in *aconitum napellus* and in *equiscetum fluviatile.* It is formed by the action of heat on citric acid, as above. To obtain it, citric acid is heated till it ceases to give off inflammable vapours, and the residue, dissolved in alcohol, is treated with hydrochloric acid gas, which causes the formation of aconitic ether. The addition of water causes this to separate, and by caustic potash it is converted into aconitate of potash. From this aconitate of lead is prepared, and this salt, decomposed by sulphuretted hydrogen, yields the acid.

It forms indistinct crystals; and although the acid thus prepared has the same composition as that from aconite, and that from equisetum, yet each of the three varieties has some peculiarities. They may not, therefore, be identical, especially as two acids derived from malic acid, the maleic and paramaleic, or fumaric acids, have the same composition. The aconitic acid from citric acid, when heated, yields itaconic and citraconic acids: it is doubtful, at present, whether the other two varieties do so.

Aconitic acid, according to the present state of our knowledge, is monobasic, and the general formula of its salts is $\overline{At}$, MO. The aconitates are not important.

When aconitic acid (from citric acid) is heated to from 356° to 392°, it boils and yields a mixture of two acids; itaconic acid, which condenses in crystals, and citraconic acid, which appears as an oily liquid. When the distillation is very rapid, itaconic acid predominates; when it is slow, there is more citraconic acid. These two acids have both the formula $C_5 H_2 O_3, HO$.

Itaconic acid is readily purified by solution in hot water, as it crystallises with great facility. It is soluble in water, alcohol, and ether. When heated it is resolved into water and anhydrous citraconic acid. It is a monobasic acid, and its formula is $C_5 H_2 O_3, HO = \overline{It}, HO$. The formula of its salts is $\overline{It}, MO$. It also forms acid salts, the formula of which is $2 \overline{It}, MO, HO$. The itaconates are not of special interest.

Citraconic acid is formed when the preceding acid is distilled, and then appears, in the anhydrous state, as a limpid oily liquid. It distils unaltered at 410°, and volatilises slowly at much lower temperatures. It attracts moisture from the air, forming a crystalline hydrate, which, when heated, is again resolved into water and anhydrous acid. The formula of the anhydrous acid is $C_5 H_2 O_3 = \overline{Ct}$; that of the hydrate $\overline{Ct}, HO$. It forms, like the preceding, both neutral and acid salts; and produces, with oxide of silver, a neutral salt with water of crystallisation; an apparently anomalous case. The formation of these two acids takes place as follows:—3 eq. of aconitic acid, $3 (C_4 H_2 O_4)$ yield 2 eq. itaconic acid, $2 (C_5 H_2 O_3, HO)$, and 2 eq. carbonic acid, $2 CO_2$. The itaconic acid, when formed, is partially resolved into water and anhydrous citraconic acid.

The three acids just described, aconitic, itaconic, and citraconic acids, require further investigation. It is probable that it will be found that they are not all monobasic. The existence of water of crystallisation in the neutral citraconate of silver is a most unusual circumstance, and would seem to indicate that we do not yet know the constitution of the acid in that salt.

2. Tartaric Acid. $C_8 H_4 O_{10}, 2 HO = \overline{T}, 2 HO$.

This acid occurs in the juice of the grape as acid tartrate of potash; also in many other plants. It is prepared from tartrate of lime, exactly as citric acid is from citrate of lime. Tartrate of lime is obtained by the action of chalk on acid tartrate of potash, or cream of tartar.

Tartaric acid crystallises in large rhombic prisms, transparent and colourless. They are very soluble in water, and have a pleasant acid taste. When boiled with alcohol, tartaric acid forms acid tartrate of oxide of ethyle. A high temperature decomposes tartaric acid, giving rise to several new products.

An excess of potash aided by heat, transforms it into acetate and oxalate of potash, $C_8 H_4 O_{10}, 2 HO = C_4 H_3 O_3, HO + 2 (C_2 O_3 HO)$. By peroxide of manganese and sulphuric acid it is converted into formic acid, carbonic acid, and other products. There is some relation between tartaric and formic acids: for if formic acid be FoO_3 ($Fo = C_2 H$), tartaric acid is $2 (Fo_2 O_5)$.

Tartaric acid precipitates lime-water white, but an excess dissolves the precipitate. In solution of potash, if the acid be added in excess, it causes a crystalline deposit of cream of tartar, which, where the potash is in very minute proportion, is rendered more visible by the addition of alcohol.

It is a bibasic acid, and forms two series of salts: 1. neutral, $\overline{T}, 2 MO$; 2. acid, $\overline{T}, MO, HO$. It forms also two kinds of double salts: in one the 2 eq. of fixed base are different protoxides, $\overline{T}, \left\{ \begin{matrix} MO \\ mO \end{matrix} \right.$; in the other, one of the equivalents of fixed base is replaced by 1 eq. of a sesquioxide; $\overline{T}, \left\{ \begin{matrix} MO \\ m_2 O_3 \end{matrix} \right.$. This latter kind may be considered basic, since the sesquioxide, $m_2 O_3$, usually neutralises as much acid as 3 eq. of protoxide. Tartaric acid is remarkable for its tendency to form double salts.

Among the neutral tartrates are, *tartrate of ammonia*, $\overline{T}, 2 NH_4 O + 2$ aq.; *tartrate of potash*, or soluble tartar, $\overline{T}, 2 KO$; *tartrate of soda*, $\overline{T}, 2 NaO + 4$ aq.; *tartrate of lime*, $\overline{T}, 2 CaO + 8$ aq., &c. &c.

Among the acid salts are, *acid tartrate of ethyle*, or tartrovinic acid, $\overline{T}, AeO, HO$—a crystallisable compound: acid tartrate of potash, or tartar, $\overline{T}, KO, HO$. This is the principal compound of tartaric acid. It exists in the juice of the grape, dissolved by the aid of the sugar present, and when that sugar is converted into alcohol, in which the tartar is insoluble, it is deposited on the sides of the fermenting casks. When purified it is quite white, and is called cream of tartar. It is much used in medicine as a safe and mild laxative. When calcined in a covered crucible it leaves a mixture of carbonate of potash and charcoal, called black flux. Hence carbonate of potash is called salt of tartar. Like all the tartrates, cream of tartar, when heated, gives off a very peculiar smell of burnt vegetable matter, peculiar to tartaric and racemic acids and their salts.

Among the very numerous double tartrates may be mentioned the *tartrate of potash and ammonia*, $\overline{T}, KO, NH_4O$: the *tartrate of potash and oxide of ethyle*, $\overline{T}, AeO, KO$; *tartrate of potash and boracic acid*, $\overline{T}, KO, BO_3$; this is the soluble cream of tartar used as a laxative on the continent:—*tartrate of potash and soda*, $\overline{T}, KO, NaO + 10$ aq. This is the salt of Seignette or Rochelle salt. It crystallises in very large transparent prisms, and is used as a mild laxative:—*tartrate of potash and peroxide of iron;* $\overline{T}, KO, Fe_2O_3$; this is the tartarised iron of the pharmacopœias:—*tartrate of potash and antimony*, $\overline{T}, KO, Sb_2O_3$. This is *tartar emetic*, one of the most valuable remedies. It must be considered as a basic salt; for Sb_2O_3, here substituted for HO or KO, in short for a protoxide, requires for its neutralisation an additional equivalent of tartaric acid. It then yields the compound $2\overline{T} + \left\{\begin{matrix}KO\\ Sb_2O_3\end{matrix}\right.$, which is neutral, since the bases contain 4 eq. of oxygen for 2 eq. of acid.

Tartar emetic is formed when 3 parts of oxide of antimony and 4 of cream of tartar are ground together, and made into a thin cream with water, which is heated to 158°, till a portion, tried separately, dissolves in 15 parts of cold water. When this is the case, 6 or 8 parts of water are added, and the whole boiled for half an hour. The liquid, filtered while hot, deposits, on cooling, crystals of tartar emetic. It forms white brilliant crystals which soon become opaque. It is soluble in 14 or 15 parts of cold water and 2 parts of boiling water. The crystals are $\overline{T}, KO, Sb_2O_3, + 2$ aq.

When heated, the crystals first lose the 2 eq. of water of crystallisation; and when the heat rises to 390°, 2 more eq. of water are given off, without the acid being destroyed. The salt is then $C_8H_2O_{10} + \left\{\begin{matrix}KO\\ SbO\end{matrix}\right.$. That is to say, 2 eq. of oxygen, from the oxide of antimony, have been expelled along with 2 of hydrogen from the acid. It has been already shown that tartar emetic $C_{12}H_4O_{10} + \left\{\begin{matrix}KO\\ Sb_2O_3\end{matrix}\right.$, contains 2 eq. of oxygen in the bases, more than is required for a neutral salt; and it is apparently these 2 eq. of oxygen which are thus expelled as water. If we bear in mind that Sb_2O_3 is the equivalent of $3KO$; or in other words, that $Sb_{\frac{2}{3}}$ is equivalent to K or to H, we can then see that the tartar emetic heated to 390° is analogous in composition to neutral tartrate of potash.

Tartrate of potash is . . . $C_8\ H_4\ O_{12} + K_2$

Tartar emetic, heated to 390° is, $C_8 \left\{\begin{matrix} H_2 \\ Sb_{\frac{4}{3}} \end{matrix}\right. O_{12} + \begin{matrix} K \\ Sb_{\frac{2}{3}} \end{matrix}$

In this point of view the 2 Sb are divided, $\frac{4}{3}$ Sb replacing hydrogen in the radical, and $\frac{2}{3}$ Sb replacing potassium in the base.

The *neutral tartrate of potash and antimony*, $2\ \overline{T}, \left\{\begin{matrix} KO \\ Sb_2\ O_3 \end{matrix}\right.$ + 7 aq. is always formed in the mother liquors of tartar emetic. It is also formed when tartar emetic is dissolved in tartaric acid.

Tartar emetic forms a double salt with cream of tartar, $\overline{T}$, $KO, Sb_2\ O_3 + 3\ (\overline{T}, KO, HO)$. It crystallises in scales.

ACTION OF HEAT ON TARTARIC ACID.

When crystallised tartaric acid is heated it melts, then loses $\frac{1}{4}$ of its water, leaving a new acid, tartralic acid; next it loses $\frac{1}{2}$ its water, and is converted into tartrelic acid; and finally it loses all its water and is converted into anhydrous tartaric acid. We may represent these changes as follows, doubling the formula of tartaric acid.

$C_{16}\ H_8\ O_{20} + 4\ HO =$ crystallised tartaric acid.
$C_{16}\ H_8\ O_{20} + 3\ HO =$ tartralic acid.
$C_{16}\ H_8\ O_{20} + 2\ HO =$ tartrelic acid.
$C_{16}\ H_8\ O_{20} =$ anhydrous tartaric acid.

In tartralic and tartrelic acids, the neutralising power is diminished, in so far that tartralic acid neutralises $\frac{1}{4}$th less base, and tartrelic acid $\frac{1}{2}$ less base than tartaric acid. Both of these acids, as well as the anhydrous acid, are, by long boiling with water, reconverted into tartaric acid. It would appear as if in the tartralic and tartrelic acids, an additional quantity of anhydrous acid had been added to the radical without affecting the neutralising power, just as in phosphoric, pyrophosphoric, and metaphosphoric acids. If we represent the anhydrous acid by $C_4\ H_2\ O_5$, then we have

$2\ (C_4\ H_2\ O_5) + 2\ HO =$ crystallised acid.
$3\ (C_4\ H_2\ O_5) + 2\ HO =$ tartralic acid.
$4\ (C_4\ H_2\ O_5) + 2\ HO =$ tartrelic acid.

When tartaric acid, or rather anhydrous tartaric acid, is more strongly heated, it yields two pyrogenous acids, one liquid, the other crystallised. The former, $C_6\ H_3\ O_5, HO$, the latter $C_5\ H_3\ O_3, HO$. In fact, 2 eq. of anhydrous tartaric acid contain the elements of 1 eq. of each of these new acids, 5 eq. of carbonic acid, and 2 eq. of water. The liquid acid is called pyroracemic acid, being obtained also from racemic acid: the solid acid may be called pyrotartaric acid.

Tartralic acid, $C_{12} H_6 O_5$, $2 HO$, is obtained by cautiously heating tartaric acid, taking care not to cause it to become brown. It is combined with baryta, and the baryta separated from the soluble tartralate by diluted sulphuric acid. Tartralic acid forms a transparent mass, not crystalline, deliquescent and soluble in alcohol. It is converted into tartaric acid, slowly by cold water, rapidly by hot water. It appears to be bibasic, and most of its salts are soluble. By long contact with water, they are converted into tartrates and free tartaric acid.

Tartrelic acid, $C_{16} H_8 O_{20}$, $2 H O$, is obtained by keeping the preceding acid long melted without raising the temperature. It is coloured brown, is deliquescent and dissolves both in water and alcohol. Water rapidly changes it into tartralic and tartaric acids. Its salts are soluble, and undergo the same change as those of tartralic acid.

Anhydrous tartaric acid, $C_4 H_2 O_5$, is prepared by rapidly heating $\frac{1}{2}$ oz. of tartaric acid in a porcelain capsule. It swells up very much, gives off water, and is at last converted into a porous white mass. This is now heated for some time, in an oil-bath, to a temperature of 302°, then powdered and well washed with cold water, and dried. It forms a white powder insoluble in water, alcohol, and ether. By the action of water and bases it is converted successively into tartrelic and tartaric acids.—*Pyroracemic acid; or liquid pyrotartaric acid*, $C_6 H_3 O_5, HO = \overline{pR}, H O$, is one of the products of the distillation of tartaric and racemic acids. It is separated from the crystals which accompany it, combined with oxide of lead, and the well-washed pyrotartrate of lead decomposed by sulphuretted hydrogen. It is concentrated in vacuo, and forms a thick syrup nearly colourless, which cannot be distilled without partial decomposition. Its salts are not easily obtained in crystals, and when their solutions are heated, they lose the power of crystallising. The general formula of the pyroracemates is $C_6 H_3 O_5, M O$. They are coloured dark-red by salts of protoxide of iron, and a crystal of sulphate of copper introduced into the solution of a pyroracemate causes a white precipitate. *Pyroracemate of oxide of ethyle* is a colourless liquid, of an aromatic smell, resembling that of *acorus*.

Pyrotartaric acid, $C_5 H_3 O_3, H O = p \overline{T}, H O$, is formed along with the preceding acid in small quantity by the distillation of tartaric acid; it is obtained far more abundantly by the distillation of cream of tartar. The product of the distillation, which is liquid, is evaporated till it crystallises, and the mother liquid, acted on by nitric acid to destroy the oily impurities, and again evaporated, yields an additional quantity. The crystals melt at 230° and volatilise at from 284° to 300°. The salts of this acid are soluble, that of lead appears to be rather sparingly so. But the results of different experimenters on this subject are so discordant that we must wait for further researches.

3. Racemic Acid. $C_4H_2O_5,HO=\overline{R},HO$? or $C_8H_8O_{10},2HO=R,2HO$?

Syn. *Paratartaric acid.*—This remarkable acid, which has the same composition in 100 parts as tartaric acid, and very similar properties, is found along with tartaric acid in the grapes of certain districts. When both acids are present, the liquid obtained by boiling the tartrate and racemate of lime with diluted sulphuric acid deposits, on evaporation, racemic acid in hard crystalline crusts, before tartaric acid, which is more soluble, begins to crystallise. It may be distinguished from tartaric acid by not forming a double salt of potash and soda.

The crystals of the racemic acid have a very sour taste, and are composed of $\overline{R}, HO+aq$. At 212° they lose the 1 eq. of water of crystallisation, and when more strongly heated, yield the same products as tartaric acid. The solution of racemic acid forms a precipitate of racemate of lime when mixed with chloride of calcium, which serves to distinguish it from tartaric acid; but like tartaric acid, it causes a crystalline precipitate in the salts of potash.

Racemic acid is possibly monobasic, and according to some, it does not, like tartaric acid, form double salts with two strong bases. It forms neutral salts, $\overline{R}, MO$, and acid salts, $\overline{R}, MO+\overline{R}, HO$. Thus the neutral racemate of potash is $\overline{R}, KO + 2$ aq., and the acid racemate of potash, analogous to cream of tartar, is $\overline{R}, KO+\overline{R}, HO$. These two salts, therefore, have precisely the same composition as the corresponding tartrates. The acid racemate of potash, with oxide of antimony, yields a double salt analogous to tartar emetic, but of a different crystalline form. The relations of racemic acid to the oxides of ethyle and methyle are similar to those of tartaric acid. On the whole, racemic acid is interesting, from its presenting one of the best marked cases of isomerism, namely with tartaric acid. In this case, not only is the composition the same, but the general properties, and most of the special ones, are identical. In fact, were it not that we must admit tartaric acid to be bibasic, we should find it difficult in any way to account for the differences which exist between the two acids. We have here, even on the supposition, which is doubtful, that racemic acid is monobasic, a very near approach to the occurrence of different properties with the same composition, and even the same arrangement. The two acid salts of potash, for example, are, on this view, $C_8 H_4 O_{10} \left\{\begin{matrix}KO\\HO\end{matrix}\right.$ for the bitartrate: and $C_4H_2O_5,KO+C_4H_2O_5,HO$ for the biracemate. If we represent the latter as follows:

$$\begin{matrix}C_4H_2O\\C_4H_2O_5\end{matrix}\left\{\begin{matrix}KO\\HO\end{matrix}\right.,$$ we see how very nearly alike they are, even on the view we have adopted of the one acid being bibasic, and the other monobasic; and we must bear in mind that these two salts are strikingly similar in properties. The same remarks apply to the crystallised acids and to the double salts with antimony, although in the case of the two acids, we have evidence of one point of difference in the arrangement. Tartaric acid is $C_8\ H_4\ O_{10},\ 2\ HO$, while racemic acid is $C_4\ H_2\ O_5,\ HO+$aq., and loses the water of crystallisation at 212°.

Fresenius has recently investigated the racemates and has not been able to establish the true distinction between racemic and tartaric acids. More recently still, a double racemate of potash and soda has been obtained, which would lead us to admit racemic acid to be, like tartaric acid, bibasic. For the present, therefore, we cannot specify with certainty any difference of constitution between the two acids.

4. Malic Acid. $C_8 H_4 O_8, 2 HO = \overline{M}, 2 HO$.

This acid is of very frequent occurrence in acid fruits, as in the apple, and especially in the unripe berries of *Sorbus aucuparia*, or mountain ash. The best method of extracting it is to express the berries when they begin to turn red, and to add to the strained liquid a thin milk of lime so as not entirely to neutralise the acid. On heating, neutral malate of lime separates, and is removed by a skimmer. To the mother liquid more milk of lime is added cautiously, so as to produce an additional quantity of salt. The malate of lime is washed with cold water, and dissolved with the aid of heat in a mixture of 1 part nitric acid, and 10 of water. On cooling, acid malate of lime is deposited in regular crystals, which are almost always colourless. They are rendered quite pure by a solution in hot water and crystallisation. From this salt, by the addition of acetate of lead, malate of lead is precipitated as a curdy white solid, which, if left in the liquid, changes into shining silky crystals. These, which are pure malate of lead, being decomposed by sulphuretted hydrogen, yield the acid, which when evaporated to a syrup forms a granular crystalline mass, deliquescent in the air, of a strong but agreeable acid taste. When the crystallised acid is kept for some time at a heat of 280°, it melts, and the melted acid is gradually filled with crystals. Cold water removes the unchanged malic acid, which, if again heated, undergoes the same change, till at length all the malic acid is converted into these crystals, which are *paramaleic* or *fumaric acid.*

If malic acid be distilled by a sharp heat, a great part passes over in the form of a volatile crystallisable acid, the *maleic acid.* At a certain period of the distillation, if the retort be removed from the fire, the boiling residue having become turbid and thick, it suddenly becomes quite solid, and is found to consist of fumaric acid.

Malic acid is bibasic; in proof of which, it forms acid salts with lime, magnesia, and oxide of zinc, which monobasic acids never do. There are two series of malates: 1. neutral, $\overline{M}$, 2 MO; 2. acid, $\overline{M}$, MO, HO. Most of the malates are soluble in water, but not in alcohol. Lime water neutralised by malic acid, continues clear whether cold or hot, which serves to distinguish it from tartaric, citric, racemic, and oxalic acids.

Acid malate of ammonia, $\overline{M}$, NH_4O, HO, is best formed by neutralising with ammonia one of two equal portions of malic acid (as prepared from the crude malate of lead by diluted sulphuric acid), and then adding the other portion and evaporating to a syrup. On cooling, large and very regular crystals of the acid salt are deposited, which are easily decolorised by animal charcoal. This is an excellent method of purifying malic acid, when it is much contaminated with other substances. *Acid malate of lime* $\overline{M}$, Ca O, HO + 6 aq., is prepared as above described. It forms very regular and pure crystals, soluble in their own weight of boiling water, but requiring 20 parts of cold water. When malic acid is saturated with chalk, an acid liquid is obtained, which, when boiled, deposits the *neutral* malate of lime, $\overline{M}$, 2 Ca O. The *malate of lead* $\overline{M}$, 2 Pb O + 6 aq. is remarkable for changing when left in the liquid in which it has been formed, from a curdy white precipitate to a mass of fine silky needles. In hot water this salt melts into a mass like pitch in consistence. *Acid malate of copper,* $\overline{M}$, Cu O, HO + 2 aq., forms splendid large crystals of a fine cobalt blue colour. There appears to be a *basic malate of copper,* $\overline{M}$, 2 Cu O + Cu O + 6 aq., which forms green crystals. *Malate of silver,* $\overline{M}$, 2 Ag O, is a white powder, soluble in boiling water. The other malates are analogous to these, and possess little interest.

Maleic Acid, $C_8H_2O_6$, 2 HO = $\overline{Ma}$, 2 HO, is prepared as above mentioned, by distilling malic acid. This acid is bibasic, but has the same composition, in 100 parts, as aconitic, or equisetic acid. It forms crystals, which are very soluble in water, alcohol, and ether. When heated sharply, it yields water, and a white volatile solid, melting at 134°, and boiling at 350°, which appears to be anhydrous maleic acid. When the hydrated acid is kept melted for some time, it is changed, exactly as malic acid is, into fumaric acid. Hydrated maleic acid has precisely the same composition as anhydrous malic acid, which at once explains its formation.

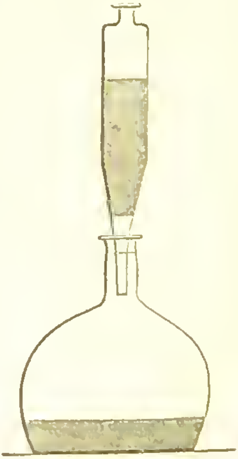
The general formula of its salts is $\overline{Ma}$, 2 M O for the neutral, and $\overline{Ma}$, M O, H O for the acid maleates. It forms an *acid maleate of silver*, $\overline{Ma}$, Ag O, H O.

Fumaric or Paramaleic Acid, $C_4\,H\,O_3$, $H\,O = \overline{Fu}$, $H O$, is formed as above stated, by heating either malic or maleic acids to their melting-point, and keeping them melted for a long time. It occurs in *fumaria officinalis*, and in Iceland moss. It forms micaceous scales requiring 200 parts of cold water for solution. It is soluble in alcohol.

It is a monobasic acid, but has the same composition in 100 parts as maleic acid, which at once explains its formation from malic, or from maleic acid. Its salts are sparingly soluble. The *fumarate of oxide of ethyle* is a heavy oily liquid of an aromatic smell of fruits. When this ether, $\overline{Fu}$, Ae O, is acted on by aqua ammoniæ, it forms a white insoluble powder, which is *fumaramide*, $C_4\,H O_2 + N H_2$. This body has all the characters of a compound amide.

5. Tannic Acid. $C_{18}\,H_5\,O_9, 3\,H\,O = Qt, 3\,H\,O$.

Syn. *Quercitannic Acid. Tannine.* This acid occurs chiefly in oak-bark and in nut-galls, an excrescence on oak-leaves caused by the attacks of an insect which apparently pierces the leaf in order to deposit its eggs.



To obtain it, coarsely-powdered nut-galls are acted on, in an apparatus of displacement by ether, free from alcohol, but saturated with water. When the ether, after being left some time in contact with the powder, is allowed to drop into the lower vessel, it separates into two strata of liquid, the lower of which is a pure solution of tannic acid in water, which is drawn off and dried up after being washed with ether. The dry mass is re-dissolved in water, and again dried up in vacuo.

Tannic acid thus obtained is nearly white, and not at all crystalline. It is very soluble in water, and has a most astringent taste without bitterness. It is soluble in weak alcohol, but hardly soluble in ether. The aqueous solution, if exposed to the air, absorbs oxygen, produces an equal volume of carbonic acid, and is converted into *gallic* and *ellagic acids.* The addition of the mineral acids to a solution of tannic acid, causes a precipitate, which is composed of tannic acid and the acid employed (sulphuric, &c.), and which is very soluble in pure water. The precipitate formed by sulphuric acid, in a hot solution, dissolves in hot diluted sulphuric acid, and when this solution has been boiled a short time, it contains no tannic acid, the whole being converted into gallic acid.

Tannic acid combines with animal gelatine, forming an insoluble curdy precipitate. A piece of prepared skin, introduced into a solution of tannic acid, absorbs the acid, and is converted into leather. When heated, tannic acid is converted into metagallic and pyrogallic acids.

Tannic acid and its salts strike a deep blue, nearly black colour with persalts of iron; and it likewise causes a precipitate in the solutions of most of the vegetable bases.

It is a tribasic acid, and the general formula for the neutral tannates is $\overline{Qt}, 3\,MO$ in the case of protoxides, and $3\,\overline{Qt}, M_2O_3$, in the case of sesquioxides. These salts, however, have been but little studied.

The conversion of tannic acid into gallic acid is not fully understood. In some circumstances, it appears to depend on the absorption of oxygen; and in fact, 1 eq. tannic acid, *plus* 8 eq. oxygen, contains the elements of 2 eq. gallic acid, 4 eq. carbonic acid, and 2 eq. water. But when the conversion is produced by sulphuric acid, no other substance is formed with the gallic acid, except a colouring matter, which appears not to be essential. There is some probability that gallic acid exists ready formed in tannic acid, and if we subtract 2 eq. anhydrous gallic acid, $2\,(C_7H_2O_4)$ from 1 eq. of hydrated tannic acid, $C_{18}H_8O_{12}$, there is left $C_4H_4O_4$, which is the composition of hydrated acetic acid; or, tripled, that of dry grape sugar. As tannic acid, or at least the powder of nutgalls, if moistened, is said to be susceptible of the vinous fermentation, it is not impossible that tannic acid may contain gallic acid, *plus* sugar, if not gallic acid, *plus* acetic acid. Tannic acid is converted into gallic acid as rapidly by the action of an excess of alkali as by that of acid; but the whole subject requires investigation.

6. Gallic Acid. $C_7 H O_3, 2 H O = \overline{G}, 2 H O$.

This acid exists in the seeds of mango, and is formed as above described by the decomposition of tannic acid. It is purified from colouring matter by combining it with oxide of lead, and decomposing the gallate of lead, suspended in water, by sulphuretted hydrogen; the sulphuret of lead acts as a decolorising agent.

Pure gallic acid forms beautiful prisms of a silky lustre, and a slight yellowish colour, of the formula $C_7 HO_3$, 2 HO+aq. It is sparingly soluble in cold water, requiring 100 parts, but dissolves in 3 parts of boiling water. Solutions of the acid and its salts, strike a black colour with persalts and protopersalts of iron. When exposed to the air, the solution of gallic acid absorbs oxygen, and becomes dark-coloured; this change is very rapid in the presence of alkalies, so that the alkaline gallates, especially if the alkali be in excess, are rapidly decomposed, and become nearly black.

When dissolved in hot oil of vitriol, and precipitated from the cold solution by water, gallic acid is obtained in a peculiar form, as $C_7 H_2 O_4$, perhaps $C_7 HO_3 + HO$, in which the crystals have lost 2 eq. of water, 1 basic or hydratic, the other, water of crystallisation. This peculiar gallic acid is a reddish-brown crystalline powder, which might be used in dyeing, as it yields colours on cloth like those from madder. When heated it forms fine red prisms, which call to mind alizarine, the crystalline matter found in madder.

By the action of heat, crystallised gallic acid yields, like tannic acid, pyrogallic and metagallic acids.

The gallates are little known. They are very easily decomposed by the action of the air. The *acid gallate of ammonia* is $\overline{G}, NH_4 O + \overline{G}$, 2 HO. Acid gallate of lead has a similar composition. There is a bibasic gallate of lead, $\overline{G}$, 2 Pb O.

The recent investigations of Büchner, jun., have shown that both the tannates and gallates are in some respects anomalous, and require further study.

When tannic, or gallic acid, is heated by a sharp fire, carbonic acid, water, and *pyrogallic acid* distil over, while a dark solid remains in the retort, which is *metagallic acid.*

Pyrogallic Acid, $C_2 HO$? $C_6 H_3 O_3$? or $C_8 H_4 O_4$? forms shining scales of a bitter and astringent taste; fusible at 240°, volatile at 410°. It is converted by a stronger heat into metagallic acid. It is formed from gallic acid, $C_7 H_3 O_5$, by the loss of 1 eq. carbonic acid. If acid at all, it is a very feeble acid, and nothing is known of its salts.

Metagallic Acid, $C_{12} H_3 O_3$, HO ? $C_6 H_2 O_2$? is produced as above mentioned from tannic, gallic, and pyrogallic acids. It is a black powder, insoluble in water, soluble in alkalies. Of its salts little is known. It differs from gallic acid only by the elements of carbonic acid ; $2 (C_7 H_2 O_4) = 2 CO_2 + C_{12} H_4 O_4$. From pyrogallic acid it only differs by the elements of water.

Tannic acid contains the elements of gallic and pyrogallic acids. $3 (C_{18} H_8 O_{12}) = 6 (C_8 H_3 O_5) + 2 (C_6 H_3 O_3)$; and since either gallic or pyrogallic acid may produce metagallic acid, it is obvious that there is a close connexion among these four compounds. The precise nature of this connexion future experiments must ascertain.

When an infusion of nut-galls has been so long exposed to the air, that all tannic acid has disappeared, the gallic acid is found mixed with an insoluble, or sparingly soluble powder, which is a new acid, *ellagic acid*. Its composition is $C_7 H_3 O_5$, and when dried at 240° $C_7 H_2 O_4$; so that it is isomeric with gallic acid, and with the modified acid produced by the action of oil of vitriol. It has not been much studied, and we do not know its actual atomic weight. When heated, it yields greenish-yellow vapours, which condense into crystals of the same colour, insoluble in water, alcohol, or ether ; soluble in sulphuric acid and in alkalies.

This acid is said to occur in the root of *Tormentilla vulgaris;* and is also the chief constituent of bezoar stones, which are a species of animal concretion. According to Mercklein and Wöhler, the acid of bezoar stones is $C_{14} H_2 O_7$ HO ; which is equal to twice the formula of ellagic acid, minus 1 eq. of hydrogen, for $2 (C_8 H_7 O_4) = C_{14} H_4 O_8$. The acids, according to Mercklein and Wöhler, are identical, and their formula, $C_{14} H_2 O_7$, $HO = C_{14} H_3 O_8$, is probably correct.

Tannic acid, and the substances derived from it, occur in a good many plants, besides those of the genus *quercus ;* the infusions of all of which are recognised by their striking a bluish-black with persalts of iron. But the astringent taste, and the property of tanning, or combining with animal gelatine, are found in many plants, such as cinchona, kino, catechu, pinus, &c. These are distinguished by giving, with persalts of iron, either a dark green or a grey colour. It has not been proved that they contain tannic acid, but Geiger has shown that these different colours may occur even when the same tanning principle is present, and that the green is owing, at all events frequently, to the presence of free acid, while the addition of chalk, in some cases, changes the green to the characteristic bluish-black due to tannic acid. There are, however, some reasons for admitting more than one tanning or astringent principle. The whole subject requires investigation.

Catechu. Mimotannic Acid.

When catechu, the dried extract of *mimosa catechu*, is acted on by cold water, it yields a soluble matter very similar to tannic acid, if not identical with it when pure. It is, however, contaminated by some compound which causes it to redden when exposed to air. It does not appear to yield the same products when heated, as tannic acid does; but this is uncertain, and may be caused by the presence of impurities. Berzelius proposes to call this tannic acid *mimotannic acid*, from *mimosa*, to distinguish it from the tannic acid of galls, which he calls *quercitannic acid*, from *quercus*.

The portion of catechu insoluble in cold water contains a peculiar compound, called *catechine* or tanningenic acid. It is soluble in hot water, and when pure forms a white silky crystalline powder, which is said to be composed of $C_{15} H_6 O_6$. When heated, it is said to be transformed into (mimo ?) tannic acid. By the action of caustic potash it yields a black acid, *japonic acid*, $C_{12} H_4 O_4, HO$? Carbonate of potash converts it into a red acid, *rubinic acid*, $C_{18} H_6 O_4$(?) in the anhydrous state. The hydrated acid is said to have the same composition as japonic acid, possibly therefore $C_{18} H_6 O_6$? But as the japonic acid, on the same authority, Svanberg, in combining with silver forms a salt $C_{24} H_8 O_7, AgO$, in which 2 eq. of the acid have lost 2 eq. of water and gained only 1 eq. oxide of silver, it is evident that our knowledge of these compounds is very imperfect.

7. Meconic Acid. $C_{14} H O_{11}, 3 HO = \overline{Mc}, 3 H O$.

A tribasic acid, found only in opium, the dried juice of *papaver somniferum*. To prepare it, the crude meconate of lime, obtained in the manufacture of muriate of morphia, is mixed with 20 parts of boiling water, and 3 parts of strong hydrochloric acid added to the mixture, which must be removed from the fire, and not boiled after the acid has been added. On cooling, acid meconate of lime is deposited in shining crystals, which are collected on a cloth filter, squeezed, and treated a second time with the same quantities of acid and hot water. The strained acid liquid contains a large but variable proportion of sulphate of lime, always present, sometimes even to the extent of ½ or ¾ in the crude meconate of lime. Hence the advantage of using so much hydrochloric acid, which also renders the meconic acid less soluble. This time the crystals are meconic acid, still much coloured. They are collected and squeezed as before, and to make sure that all lime is removed, a third time dissolved in 20 parts of hot water and 2 of hydrochloric acid. The addition of the acid not only removes the last traces of lime, but causes the meconic acid to crystallise almost entirely out of the liquid, it being nearly insoluble in diluted acid. The crystals, washed with a little cold water, and dried at the ordinary temperature, are now pure from everything but colouring matter, and when heated to redness leave no residue.

To get rid of the colour, the crystals are now mixed with warm water, and caustic potash gradually added, so as nearly but not quite to neutralise the acid. As soon as the point of neutralisation is reached, the reddish colour changes to green, and so much potash must be added that any further quantity would produce the green colour. The whole is then heated in the water bath, till all is dissolved, hot water being added, if necessary. (Were the potash now in excess, the whole acid would be decomposed into oxalic and carbonic acids.) On cooling, the meconate of potash, $\overline{\mathrm{Me}}\left\{\begin{array}{l}2\,KO\\ HO\end{array}\right.$, crystallises, forming a semi-solid mass, which is to be squeezed out. The colour is carried off for the most part in the mother liquor, which is very dark, and the squeezed salt, after a second, or if necessary a third, solution in hot water, crystallisation, and squeezing, is snow-white. This purified meconate of potash is then acted on by pure hydrochloric acid, exactly as recommended for the meconate of lime, and after the third operation yields perfectly pure and white meconic acid in beautiful silvery scales, which, to remove any traces of the acid mother liquid adhering to them, may be once more dissolved in the smallest possible quantity of hot water, avoiding a heat of 212°, which decomposes the acid; the pure acid is deposited on cooling, as $\overline{\mathrm{Me}}$, $3\,HO + 6\,aq$.

Meconic acid, when gently heated, loses 6 eq. of water of crystallisation. It is soluble in water and in alcohol. When boiled, its solution becomes coloured, producing comenic acid, carbonic acid, and a dark-brown colouring matter. If boiled with hydrochloric acid, it is resolved into comenic acid and carbonic acid, without the production of colouring matter. When the dry acid is heated to 250°, the same change takes place. When heated with excess of aqua potassæ, meconic acid is entirely decomposed into oxalic acid, carbonic acid, and a dark colouring matter. Its distinguishing character is that of causing, in persalts of iron, a deep blood-red colour, but no precipitate.

It forms three series of salts, like other tribasic acids. Thus, there are three meconates of potash: 1. acid, $\overline{Me}, \left\{\begin{matrix} KO \\ 2\,HO \end{matrix}\right.$; 2. Neutral, above mentioned, $\overline{Me} \left\{\begin{matrix} 2\,KO \\ HO, \end{matrix}\right.$ aq. Both of these crystallise. 3. tribasic, $\overline{Me}, 3\,KO$. This is yellow, and does not crystallise. There are also three meconates of soda; two of lime, acid and neutral or bibasic, and two of silver, bibasic $\overline{Me}, 2\,AgO, HO$, and tribasic $\overline{Me}, 3\,AgO$. The meconate of peroxide of iron is very soluble, of an intense blood-red colour, but as it cannot be obtained pure or crystallised, its composition is still unknown.

8. Comenic Acid. $C_{12}H_2O_8, 2\,HO = \overline{Co}, 2\,HO$.

This acid is formed as above described, from meconic acid by the action of heat, or of heat and an acid combined. 1 eq. dried meconic acid, $C_{14}\,HO_{11} + 3\,HO = C_{14}\,H_4\,O_{14}$, yields 1 eq. comenic acid, $C_{12}\,H_2\,O_8, 2\,HO$, and 2 eq. carbonic acid, $2\,CO\,2$. The acid is readily obtained by boiling meconate of lime with an excess of diluted hydrochloric acid. It is deposited on cooling in coloured crystals, which may be decolorised by recrystallisation with the aid of animal charcoal. The pure acid has a slight yellow tinge, and is very sparingly soluble in cold water. When heated, it is resolved into carbonic acid, *pyromeconic acid*, and a small quantity of a third substance, *paracomenic acid*, which, in some few points, differs from comenic acid, but has the same composition, and in many points is so similar that it may possibly turn out to be essentially the same.

Comenic acid forms two series of salts, with 1 and 2 eq. of fixed base respectively. With persalts of iron it forms a deep red solution which deposits black crystals of unknown composition.

Pyromeconic Acid, $C_{10}\,H_3\,O_5, HO$, is obtained as a crystalline sublimate by heating meconic or comenic acids. In fact 1 eq. comenic acid, $C_{12}\,H_4\,O_{10}$, contains the elements of 1 eq. pyromeconic acid, $C_{10}\,H_4\,O_6$, and 2 eq. carbonic acid, $2\,CO_2$. It forms very soluble four-sided prisms, rather styptic to the taste; the solution of which forms with persalts of iron a crystalline salt of a fine red colour, the powder of which is like vermilion. This salt is $Fe_2\,O_3 + 3\,C_{10}\,H_3\,O_5$. Pyromeconic acid is so feeble an acid, that we can hardly class it with acids. It has more analogy with such bodies as acetone, derived from acetic acid, as pyromeconic acid is from meconic or comenic acid. It has the same composition as pyromucic acid.

9. Kinic Acid. $C_7H^4O_4, 2HO$? or $C_{14}H_{11}O_{11}, HO$?

This very remarkable acid occurs in cinchona bark. It is obtained in the manufacture of sulphate of quinine, in the form of kinate of lime, from which the lime is easily separated by means of oxalic acid. The liquid filtered from the oxalate of lime yields, on evaporation, the kinic acid in crystals. The lime may also be removed by sulphuric acid, and any adhering sulphate of lime separated by alcohol.

The salts of kinic acid are somewhat anomalous. Thus there is a salt of lead, $C_7H_4O_4\ 2PbO$, and a salt of copper, $C_7H_4O_4, CuO, HO$, while the crystals of kinic acid are $C_7H_6O_6$. All this would lead to the conclusion that the acid was a bibasic one, $C_7H_4O_4, 2HO$. But the kinate of lime, and the kinate of silver, both quite neutral salts, are $C_{14}H_{11}O_{11}, CaO$, and $C_{14}H_{11}O_{11}, AgO$, as if the acid were monobasic, $C_{14}H_{11}O_{11}, HO = C_{14}H_{12}O_{12}$. If we assume the acid to be quadribasic, we can then bring all the above salts into one series.

Thus,—Kinic acid would be .	$C_{14}H_8O_8, 4HO$
Kinate of lead . . .	$C_{14}H_8O_8, 4PbO$
Kinate of copper . .	$C_{14}H_8O_8,\left\{\begin{matrix}2\,CuO\\2\,HO\end{matrix}\right.$
Kinate of lime . .	$C_{14}H_8O_8,\left\{\begin{matrix}CaO\\3\,HO\end{matrix}\right. + 10\,aq.$
Kinate of silver . .	$C_{14}H_8O_8,\left\{\begin{matrix}AgO\\3\,HO.\end{matrix}\right.$

But the objection to this view is that, if this be the true constitution of the acid, the salts of lime and silver ought to be very acid, instead of being quite neutral.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

When kinic acid or kinate of lime is distilled with diluted sulphuric acid and peroxide of manganese, there is obtained a new compound called *kinone*, as a sublimate of fine golden yellow crystals, soluble in water, and very volatile, having a pungent smell in the state of vapour. Their composition is $C_{25}H_8O_8$. When acted on by reducing agents, it takes up 2 and 4 eq. of hydrogen, forming two new compounds, green and white hydrokinone. The *green hydrokinone*, $C_{25}H_{10}O_8$, is one of the most beautiful compounds known to chemists, forming long prisms of the most brilliant gold-green metallic lustre, surpassing those of murexide in beauty. It is best formed by adding a few drops of sulphurous acid to a solution of kinone. When an excess of sulphurous acid is used, the *white hydrokinone*, $C_{25}H_{12}O_8$, is formed, which crystallises in six-sided prisms.

When acted on by oxidising agents, the solution of white hydrokinone becomes dark-red, nearly black, and almost immediately deposits the splendid crystals of the green compound. The latter is also formed by simply mixing solutions of kinone and white hydrokinone, being intermediate in composition between those bodies. Wöhler, to whom we are indebted for most of our knowledge in regard to these very curious compounds, has described a series of bodies obtained from the above by the action of hydrochloric acid, chlorine, and sulphuretted hydrogen. The following tabular view contains the names and composition of these substances, as far as we yet know them.

Kinone	C_{25}	H_8	O_8
Green hydrokinone . . .	C_{25}	H_{10}	O_8
White hydrokinone . . .	C_{25}	H_{12}	O_8
Chlorohydrokinone . . .	C_{25}	$\left\{\begin{matrix}H_{10}\\Cl_2\end{matrix}\right.$	O_8
Chlorokinone	C_{25}	$\left\{\begin{matrix}Cl_2\\H_6\end{matrix}\right.$	O_8
Brown sulphohydrokinone . .	C_{25}	H_{11}	$O_7\ S_4$
Yellow ditto . . .	C_{25}	H_{12}	$O_7\ S_5$
Brown Chlorosulphokinone . .	C_{25}	$H_8\ Cl$	$O_8\ S_4$?
Orange ditto . . .	C_{25}	$H_6\ Cl$	$O_8\ S_4$?

It will be observed, that in all these formulæ the carbon remains unaltered, and that several are instances of pure substitution, as $C_{25}\ H_8\ O_8$, compared with $C_{25}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right. O_8$, and $C_{25}\ H_{12}\ O_8$, compared with $C_{25}\left\{\begin{matrix}H_{10}\\Cl_2\end{matrix}\right. O_8$. We can also see the relation of the sulphohydrokinones to kinone if we express them as follows:—$C_{25}\ H_8\left\{\begin{matrix}O_7\\S\end{matrix}\right. + 3\ HS$; and $C_{25}\ H_8\left\{\begin{matrix}O_7\\S\end{matrix}\right. + 4\ HS$.

We now come to a class of acids of very distinct and peculiar characters; those, namely, which occur as the chief constituents of fat oils and fats, vegetable or animal. Of these oily acids there are two kinds: 1. those which are volatile, and usually somewhat soluble in water; 2. those which have more the character of the oils and fats from which they are derived, and can seldom be distilled without decomposition. We shall begin with the volatile oily acids.

10. Butyric Acid. $C_8\ H_7\ O_3,\ HO$.

This acid exists in small proportion in butter, in the form of a neutral *butyrate of glycerine*, or *butyrine*, to which the butter owes its peculiar and agreeable flavour. When butter is saponified by potash, and the solution of the soap is decomposed by tartaric acid, the oleic and margaric acids are separated as an oily stratum, while three or four volatile acids are dissolved in the water. These are butyric, caproic, capric, and caprylic acids. The butyric acid may be extracted from the mixture; but it is far better obtained by the fermentation of sugar. When sugar, either cane, grape, or milk sugar, is mixed with cheese, water, and chalk, and kept in a warm place, lactic acid is at first formed, which combines with the lime. But if the fermentation be continued at a pretty high temperature, 90° to 100° for example, the lactate of lime disappears, and is at last replaced by butyrate of lime, as explained under the head of butyric fermentation. This salt is now distilled with diluted hydrochloric acid, and the distilled liquid treated with chloride of calcium, when it divides into two strata. The lighter is butyric acid, still containing water. It is rectified until the boiling point rises to 318°. The previous portions contain water; what now passes is pure.

Bensch recommends to convert the butyrate of lime, by the addition of carbonate of soda, into butyrate of soda, and to mix the solution of this salt with sulphuric acid diluted with an equal weight of water, when the greater part of the crude butyric acid rises to the surface, and may be removed by a pipette. The acid solution of sulphate of soda, being distilled, yields an additional quantity of diluted butyric acid, which is saturated with soda, and the salt decomposed by sulphuric acid, which yields a second portion of crude butyric acid. The whole of the crude acid is now purified by rectification.

It is a clear, colourless, mobile liquid of an odour resembling that of acetic acid and that of butter. An intense cold solidifies it. It is very acid and corrosive. Its Sp. G. is 0·963. It dissolves fats and fat oils.

Chlorine decomposes butyric acid, producing by substitution two acids, $C_8 \left\{ \begin{matrix} H_5 \\ Cl_2 \end{matrix} \right. O_3, HO$; and $C_8 \left\{ \begin{matrix} H_3 \\ Cl_4 \end{matrix} \right. O_3, HO$. The latter crystallises; and both form volatile fragrant compounds with oxide of ethyle.

Butyrate of lime is remarkable as being very soluble in cold water, but separating from the liquid in transparent prisms when it is boiled. *Butyrate of baryta*, when placed on the surface of water, exhibits the same motions as camphor. *Butyrate of oxide of ethyle* or butyric ether, $AeO, C_8H_7O_3$, is formed with singular facility by the mere mixture of alcohol and butyric acid with water and sulphuric acid. It rises to the surface as a very mobile liquid of an odour somewhat similar to that of pine-apples. It is very soluble in alcohol. This ether is employed to flavour spirits: and there is reason to believe that the peculiar flavour of rum depends on the presence of a little butyric ether. *Butyrate of oxide of methyle* is quite analogous. *Butyrate of oxide of glyceryle* or *Butyrine* exists in butter, and is supposed to be capable of being formed artificially, by warming a mixture of butyric acid, glycerine, and sulphuric acid. If the oil thus formed is really butyrine, it will be the first example of a compound of glycerine formed or reproduced artificially.

Butyramide, $C_8 H_7 O_2 + N H_2$ is formed when liquid ammonia acts on butyric ether. $Ae O, C_8 H_7 O_3 + N H_3 = Ae O, H O + C_8 H_7 O_2, N H_2$. It crystallises in pearly scales.

Butyrone, $C_7 H_7 O$, analogous to acetone, is formed along with carbonate of lime, when butyrate of lime is distilled. $C_8 H_7 O_3, Ca O = C_7 H_7 O + Ca O, C O_2$. By the action of nitric acid, butyrone is converted into two new compounds; one, an ethereal fragrant liquid, lighter than water, the composition of which is not yet known: the other, an oily liquid, heavier than water, of an aromatic smell and a sweet taste, which is an acid, *nitrobutyric or butyronitric acid.* It is formed by substitution of $N O_4$ for H; $C_7 \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right. O, 2 H O$ from $C_7 H_7 O$. It forms crystallisable salts, and is bibasic, yielding two salts with oxide of silver, with 1 and 2 eq. of that oxide respectively.

By distillation with perchloride of phosphorus, butyrone is converted into an ethereal liquid, chlorobutyrene, the composition of which is $C_{14} H_{13} Cl$.

The caproic, capric and caprylic acids found in butter, are very analogous to butyric acid, but are not yet so well known. *Caproic acid* is $C_{12} H_{11} O_3, H O$. Its odour is like that of sweat. *Caproate of oxide of ethyle* has an odour somewhat analogous to that of butter. *Capric acid* is $C_{20} H_{19} O_3, H O$. It is very analogous to the preceding, but its odour is more like that of the goat. *Caprylic acid* is $C_{16} H_{15} O_3, H O$, and it is very analogous to the others.

It occasionally happens that butter, instead of yielding a mixture of volatile oily acids, of which butyric and caproic acid constitute the principal part, gives a mixture devoid of these acids, but containing in their place another acid, vaccinic acid, which is easily transformed into the other two. There can be no doubt that it contains the elements of butyric and caproic acids, $C_8 H_7 O_3, H O + C_{12} H_{11} O_3, HO = C_{20} H_{20} O_8$, or possibly $C_{20}H_{19}O_7 = C_{20}H_{18}O_6, HO$. In the latter case, it would require 1 eq. of water to yield the other acids. As, however, the solution remains neutral when vaccinic acid passes into caproic and butyric acids, it is most probably bibasic, $C_{20}H_{18}O_6, 2\,HO$, and is, in fact, the sum of the other two. The cause of its occurrence is unknown.

Oenanthylic Acid, $C_{14}H_{13}O_3, HO$, is formed by the action of nitric acid on castor oil, and has lately been detected by Redtenbacher among the products of the action of nitric acid on oleic acid, along with acetic, metacetonic, butyric, valerianic, caproic, caprylic, pelargonic and capric acids, all belonging to the series represented as hydrates by $(C\,H)\,n + O_4$, of which a table has been given at p. 260.

This acid, in composition, as well as in properties, is exactly intermediate between caproic and caprylic acids.

Oenanthole. According to Bussy, when castor oil is distilled, there is formed a neutral oil, which he calls œnanthole, the formula of which is $C_{14}H_{13}O, HO$, and which bears to œnanthylic acid the same relation as aldehyde to acetic acid. It may also be viewed, doubling its formula, as a compound of œnanthylic acid with the oxide $C_{14}H_{15}O$, (analogous to oxide of ethyle), and in this view it corresponds to acetic ether, which is polymeric with aldehyde; thus, $2\,C_{14}H_{13}O, HO = C_{14}H_{15}O + C_{14}H_{13}O_3$. Cetine (spermaceti) is an analogous compound, being either, as formerly explained, cetylate of oxide of cetyle, $C_{32}H_{33}O + C_{32}H_{31}O_3$, or $C_{32}H_{31}O, HO$, analogous to aldehyde. In the cases of œnanthole and cetine, as only one compound is known, we cannot with certainty say whether the known compound corresponds to aldehyde or to acetic ether; but it is highly probable that in the case of all the acids of the series $(C\,H)\,n + O_4$, both the compound analogous to aldehyde, and that analogous to acetic ether, are capable of existing. The following comparison will show the analogy :—

Acids.		Aldehydes.	Ethers.
Acetic	$C_4H_3O_3,HO$;	C_4H_3O,HO;	$C_4H_5O, C_4H_3O_3$;
Oenanthylic	$C_{14}H_{13}O_3,HO$;	$C_{14}H_{13}O,HO$? Oenanthole.	$C_{14}H_{15}O, C_{14}H_{13}O_3$?
Cetylic	$C_{32}H_{31}O_3,HO$;	$C_{32}H_{31}O,HO$?	$C_{32}H_{33}O, C_{32}H_{31}O_3$? Cetine.

It will be observed, that the compounds in the second and third columns are, in each case, polymeric.

Pelargonic Acid, $C_{18} H_{17} O_3 HO$. This acid, which belongs to the series above mentioned, and stands between caprylic and capric acids, is said to occur in the juice of *Pelargonium roseum,* and was found by Redtenbacher among the products of the oxidation of oleic acid by nitric acid. It is little known.

Hircic Acid is probably a mixture of capric and caprylic acids. *Phocenic acid,* found in small quantity in the oil of the dolphin, &c., has been found to be identical with valerianic acid.

Cevadic Acid is a crystalline volatile acid, obtained from the seeds of *Veratrum sabadilla:* composition unknown.

Veratric Acid is contained in the same seeds. It is solid, crystallisable, and volatile. Its formula is $C_{18} H_9 O_7$, HO. It forms a crystalline ether with oxide of ethyle; AeO, $C_{18} H_9 O_7$.

Crotonic Acid is another solid volatile acid, found in the seeds of *Croton tiglium.* It has a pungent, acrid taste, and a nauseous smell. It forms crystallisable salts.

11. Camphoric Acid. $C_{10} H_7 O_3, HO = \overline{Ca}, HO$.

This acid is formed by the action of nitric acid on camphor. It forms crystalline scales, sparingly soluble in cold water, very soluble in alcohol and ether, fusible at 158°. These are the hydrated acid, which, if distilled, is resolved into water and anhydrous camphoric acid. The camphorates are not peculiarly interesting. With oxide of ethyle, camphoric acid forms two compounds: 1. neutral, or *camphoric ether,* $\overline{Ca}$, AeO, an oily liquid, of a bitter taste and nauseous smell. 2. acid, 2 $\overline{Ca}$, AeO, HO, also called camphovinic acid, as it forms double salts, 2 $\overline{Ca}$, AeO, MO. When chlorine acts on camphoric ether, $\overline{Ca}$, $C_4 H_5 O$, it gives rise to the compound $\overline{Ca}, C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right. O$.

Anhydrous camphoric Acid, $C_{10} H_7 O_3$, forms, with bases, salts different from those formed by the hydrated acid. It is probable that it still retains some water replaceable by bases, being perhaps $C_{10} H_6 O_2$, HO; or it may differ from ordinary camphoric acid as metaphosphoric acid does from common phosphoric acid. It is solid, crystalline, and volatile, and with dry ammonia forms a compound from which potash disengages no ammonia: with liquid ammonia it yields a salt different from camphorate of ammonia. Its action on oxide of ethyle has not been studied; but the subject deserves investigation.

By the action of sulphuric acid on anhydrous camphoric acid, there is formed, with disengagement of carbonic oxide, a new acid, *sulphocamphoric acid* $(C_9 H_7 O_3, SO_2) HO+2$ aq. This acid is crystallisable, and forms crystallisable salts of the formula $(C_9 H_7 O_3, SO_2) MO=C_9 H_7 SO_5, MO$.

CAMPHOR.

There are two kinds of camphor: that of Japan, or common camphor, $C_{10} H_8 O$; and that of Borneo, $C_{10} H_9 O$, or $C_{20} H_{18} O_2$. The properties of common camphor, and its peculiar smell, are well known. Its Sp. G. is 0·985 to 0·996; it is very volatile, evaporating at ordinary temperatures. Small fragments of camphor, on the surface of water, evaporate more rapidly, with rotatory movements. It dissolves in alcohol, and is precipitated by water. When distilled with anhydrous phosphoric acid, it yields a carbo-hydrogen, called camphogen, $C_{20} H_{14}$.

When camphor is passed in vapour over a heated mixture of hydrates of potash and lime, it yields a new acid, *campholic acid*, $C_{20} H_{17} O_3$, HO. Nitric acid, with the aid of heat, converts camphor into camphoric acid. The *essence or oil of camphor* of commerce is $C_{20} H_{16} O=2$ eq. camphor *minus* 1 eq. oxygen.

Borneo camphor occurs in small crystalline fragments. Its odour is different from that of common camphor. I find that, if wrapped in paper, a distinctly alliaceous odour traverses the paper, and may thus be detected. Heated with phosphoric acid, it yields a carbo-hydrogen, $C_{20} H_{16}$; and this is also the composition of the essence which accompanies Borneo camphor. This essence is, therefore, Borneo camphor, $C_{20} H_{18} O_2$, minus 2 eq. water.

Common camphor is produced by the *Laurus camphora*; Borneo camphor is the produce of *Dryobalanops camphora*, and is, for some unknown reason, so highly prized by the Japanese, that it is not found in the markets of Europe.

Camphogen, $C_{20} H_{14}$, is the name given to the carbo-hydrogen obtained when common camphor is distilled with dry phosphoric acid. It occurs naturally in the oil of cumin. When acted on by sulphuric acid, it forms a new acid, *sulphocamphic* or *hyposulphocamphic acid*, $C_{20} H_{13} S_2 O_5$, HO.

When camphor is passed over red-hot lime, another new compound is formed, namely, *camphrone*, $C_{30} H_{21} O=3 (C_{10} H_8 O)-H_3+O_2$. At a white heat camphor yields naphthaline, carburetted hydrogen, and carbonic oxide. 4 eq. camphor contain the elements $(C_{40} H_{32} O_4)$ of 1 eq. naphthaline,

$C_{20}H_8$; olefiant gas, $2\,C_4H_4$; marsh gas, $8\,C\,H$; and carbonic oxide, $4\,CO$.

12. Valerianic Acid. $C_{10}H_9O_3, HO = \overline{Va}, HO$.

This acid has already been mentioned as produced from hydrated oxide of amyle. It also occurs in the root of valerian. It forms two hydrates, $\overline{Va}, HO$, and $\overline{Va}, HO + 2\,aq$.

The general formula of the valerates is $\overline{Va}, MO$. *Valerate of oxide of ethyle*, $\overline{Va}, AeO$, is an oily liquid, of a smell like that of fruits and that of valerian at the same time.

By the action of chlorine, valerianic acid yields two new acids: 1. *Chlorovalerisic acid*, $C_{10}.\left\{\begin{matrix}H_6\\Cl_3\end{matrix}\right.O_3, HO$. 2. *Chlorovalerosic acid*, $C_{10}\left\{\begin{matrix}H_5\\Cl_4\end{matrix}\right.O_3, HO$. Both these compounds are formed by substitution without change of type.

When valerate of lime is distilled, it is said by Löwig to yield a volatile oily compound, valerone, $C_9H_9O = C_{10}H_9O_3 - CO_2$.

13. Anisic Acid. $C_{16}H_6O_5, HO$.

This acid is obtained when the concrete essence of aniseseed is acted on by nitric acid. It is crystallisable and volatile, and forms salts which crystallise readily. When heated with an excess of baryta, it yields an oily liquid, called *anisole*.

The prolonged action of nitric acid on the concrete essence of anise produces another acid, *nitro-anisic acid*, in small yellow crystals. Its formula is $C_{16}H_5NO_9, HO = C_{16}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right.O_5, HO$. It is now found to be identical with nitrodraconic acid.

Anisole, the product formed when anisic acid is heated with baryta, is composed of $C_{14}H_7O_2 = C_{16}H_6O_5, HO - 2\,CO_2$. It is formed, also, when the salicylate of oxide of methyle is heated with baryta. By the action of bromine, anisole gives rise to two new products, in which 1 and 2 eq. of hydrogen are respectively replaced by bromine ; $C_{14}\left\{\begin{matrix}H_6\\Br\end{matrix}\right.O_2$ and $C_{14}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right.O_2$. The latter is crystalline. Nitric acid acts violently on anisole, forming a crystalline mass, which dissolves in alcohol, with a rich green colour, but is deposited in colourless needles, corresponding to one of the bromine compounds. Fuming sulphuric acid dissolves anisole, producing two compounds ; one, insoluble in water, analogous to sulphobenzine; the other, soluble, an acid analogous to sulphovinic acid. $2\,SO_3 + C_{14}H_7O_2, HO$.

Anisole, $C_{14}H_7O_2$, contains 1 eq. of hydrogen more than hyduret of benzoyle, $C_{14}H_5O_2$, H.

14. Œnanthic Acid. $C_{14}H_{13}O_2,HO$.

This acid, in combination with oxide of ethyle, forming œnanthic ether, is found in wine, in the oil of grain spirit, and in some other fermented liquors. It is, as œnanthic ether, the cause of that peculiar odour of wine which adheres so remarkably to vessels in which wine has been kept, and enables us at once to say that an empty bottle or cask has contained wine. To obtain the acid, the ether is decomposed by caustic potash, and the œnanthate of potash distilled with dilute sulphuric acid. The hydrated acid is semisolid like butter, and is, in fact, a fat oil, insoluble in water, soluble in alcohol and ether.

Of its salts, the *œnanthate of oxide of ethyle*, œnanthic ether, is best known. It is a colourless liquid, of a peculiar vinous smell, which, when strong, has a stupifying effect. When hydrated œnanthic acid is distilled, it yields water, and anhydrous acid, more solid than the hydrate.

15. Roccellic Acid. $C_{17}H_{15}O_3,HO$?

This acid occurs in *Rocella tinctoria.* It is crystallisable, insoluble in water, soluble in alcohol and ether. It has most of the properties of a fat acid, and its salts with the alkalies resemble soaps.

16. Cuminic Acid. $C_{20}H_{11}O_3,HO$.

This acid is formed from the essential oil of cumin by oxidation with hydrated alkalies. It forms tabular crystals of singular beauty. It is fusible and volatile, insoluble in cold water, soluble in alcohol and ether. When heated with caustic baryta, it yields a carbo-hydrogen, analogous to benzole, which is called *cumene.*

It forms well-defined salts with bases. Cuminate of oxide of ethyle, formed by passing hydrochloric acid gas through a solution of cuminic acid in alcohol, is an ethereal liquid, of a fragrant smell like that of apples.

Cumene, obtained by heating cuminic acid with baryta, is a colourless liquid of a sweet smell. It is formed from cuminic acid, $C_{20}H_{12}O_4$, by the loss of 2 eq. carbonic acid, exactly as benzole is formed from benzoic acid; and its formula is consequently $C_{18}H_{12}$. Both nitric and sulphuric acid act on it and form new compounds, not yet fully examined. That formed by sulphuric acid is an acid, sulphocuminic acid, $C_{18}H_{11}$, S_2O_5+HO.

Essence of cumin (*Cuminum cyminum*) contains two oils: 1. Cuminole, $C_{20}H_{12}O_2$, which is the true oil of cumin, analogous to hyduret of benzoyle; 2. Cymene, $C_{20}H_{14}$, isomeric with camphogen. It is an oil of an agreeable odour of lemons. The oil is acted on by nitric and sulphuric acids, which produce two new acids. That formed with sulphuric acid is $C_{20}H_{13}, S_2O_5, HO$.

Cuminole, $C_{20}H_{12}O_2$, may be viewed as analogous to hyduret of benzoyle, in which case it becomes $C_{20}H_{11}O_2+H$, the hyduret of a new radical, *cumyle*. Cuminic acid then becomes $C_{20}H_{11}O_2, O+HO$, analogous to benzoic acid. Chlorine acts on hyduret of cumyle, producing a compound, $C_{20}H_{11}O_2, Cl$, which is chloride of cumyle. Adopting the symbol $Cm=C_{20}H_{11}O_2$, we have CmH, $CmO+HO$, and $CmCl$, analogous to BzH, $BzO+HO$, and $BzCl$.

17. Eugenic Acid. $C_{20}H_{12}O_4$? or $C_{20}H_{13}O_5$?

This acid is found in cloves, along with a neutral oil, $C_{10}H_8$, or $C_{20}H_{16}$. The latter is separated by potash, and the eugenic acid obtained by distilling the salt of potash with dilute sulphuric acid. It is an oily liquid, of Sp. G. 1·079, having the strongest odour of cloves. It forms crystallisable salts with bases, and among them an acid salt of potash, $2\,C_{20}H_{12}O_4+KO+HO$?

Cloves, likewise, contain two crystallisable compounds: 1. *Caryophylline*, which forms yellow prisms; of the formula $C_{20}H_{16}O_2$, an oxide, therefore, of the neutral oil of cloves. 2. *Eugenine*, which forms yellow pearly scales, the composition of which is the same as that of eugenic acid.

18. Cocinic Acid. $C_{26}H_{25}O_3, HO$.

This acid, the first of the proper fat acids which we have come to, is found in the butter of the cocoa-nut combined with glycerine. The butter is saponified by potash, and the soap produced is decomposed by a mineral acid, when the fatty acid rises to the surface. It is purified by being again saponified, and finally by crystallisation in alcohol. It forms snow-white crystalline scales, fusible at 95°, and volatile. The salts of this acid with the alkalies are soaps like those of all fatty acids. *Cocinate of oxide of ethyle* is a colourless ether, with a very fragrant smell of apples. Cocinic acid belongs to the series $(CH)n+O_4$.

19. Myristic Acid. $C_{28}H_{27}O_3, HO$.

This acid, which also belongs to the series $(CH)n+O_4$, is found combined with glycerine, as a fat or butter, in the berries of *Myristica moschata* or nutmeg. There are two fats in the seeds, one red and unctuous, the other, myristine, white, and crystalline. It is easily purified by dissolving it in hot alcohol, in which it is, like the cocinate of glycerine, very soluble. On cooling, the pure myristine or myristate of glycerine is deposited as silky needles, which being saponified by potash, and the soap decomposed by an acid, yield myristic acid. The acid is purified by means of alcohol. It melts at 118°, and is decomposed by distillation.

The salts of this acid with the alkalies are soaps: very soluble in alcohol; and their aqueous solutions do not become viscid or ropy when concentrated. *Myristate of oxide of ethyle* is a colourless oil. Myristate of oxide of glyceryle or *myristine* is purified as above described. It is a beautifully crystalline fat, melting at 88°. It is saponified with difficulty, and only by fusion with solid potash. It does not appear to contain ordinary glycerine: at least its formula would indicate a glycerine composed of $C_3\,H_2\,O$. This point is at present very obscure.

The formula of hydrated œnanthic acid, doubled, or $C_{28}\,H_{28}\,O_6$, contains 2 eq. of oxygen more than 1 eq. of hydrated myristic acid, $C_{28}\,H_{28}\,O_4$; or the formula of dry œnanthic acid doubled, $C_{28}\,H_{26}\,O_4$, contains 1 eq. of hydrogen less and 1 eq. of oxygen more than dry myristic acid, $C_{28}\,H_{27}\,O_3$.

20. Palmitic Acid. $C_{32}\,H_{31}\,O_3,\,HO$.

This is the principal fat acid of palm oil. It is extracted by the usual process for fatty acids, and purified from oleic acid by crystallisation in alcohol. It forms brilliant scales, similar to margaric acid, and melting at the same point, 140°, as that acid. It may be distilled in great part unchanged. Chlorine decomposes it, giving rise to new compounds.

The salts of this acid with the alkalies are soaps, and palm oil is much used in soap-making. Palmitate of glycerine, or palmitine, is the fat or butter of the palm oil, purified from the oleine or liquid part, by pressure, and then by crystallisation in ether. It melts at 118°, and on cooling assumes the aspect of wax. Like myristine, it appears to contain the modified glycerine $C_3\,H_2\,O$, or oxide of lipyle, which is $\frac{C_6\,H_7\,O_5 - 3\,HO}{2}$; that is, glycerine, minus 3 eq. of water, and divided by 2. Pure palmitine (as also pure myristine), when distilled, yields *acroleine*, derived from the glycerine; but no sebacic acids The crude palm oil, or impure palmitine, however, yield.

abundance of sebacic acid, a compound derived from oleic acid, and proving, therefore, the presence of oleic acid or rather oleine.

21. Cetylic Acid. $C_{32} H_{31} O_3, HO$.

Syn. *Ethalic Acid.* This acid, which is isomeric with the preceding, is formed when ethal (hydrated oxide of cetyle) is heated with hydrates of lime and potash, or when cetine (spermaceti, cetylate of oxide of cetyle) is fused with potash, and the cetylate of potash decomposed by a stronger acid. It belongs of course, with the preceding acid, to the series $(CH) n + O_4$. It is separated as usual in the case of fatty acids. It is a solid, fusible between 130° and 140°, and at 131° solidifying in radiated groups of needles. It may be distilled unaltered. Its salts are like those of the preceding acids.

22. Margaric Acid. $C_{34} H_{33} O_3, HO$; or, $C_{68} H_{66} O_6, 2HO$.

This is one of the most abundant and important of the fatty acids. Combined with glycerine, or margarine, it occurs in human fat and some other animal fats, and in many vegetable fats, such as olive oil. The acid may be extracted from soap made of these fats, but as it is mixed with much oleic acid, it is better to prepare it by oxidising stearic acid (see below) by nitric acid, or by distilling either tallow or crude stearic acid. In the latter case, the product is well squeezed and purified by solution in alcohol, and crystallisation. If prepared from pure stearic acid by nitric acid, it is pure from the first. It belongs to the series $(CH)n + O_4$, and it is probably in consequence of its composition, that, like the other acids of that series, it is volatile without decomposition.

Margaric acid is a white solid fat, of distinct acid properties, fusible at 140°, very soluble in hot alcohol and in ether. It instantly combines with bases, decomposing the carbonates and forming perfect soaps with potash and soda. The neutral margarates of potash and soda are decomposed by the addition of much water, depositing the acid margarates in pearly scales. *Margarate of glycerine*, or *margarine*, is found pure in the solid part of human fat or of olive oil. It dissolves in hot alcohol, and crystallises on cooling. *Margarate of oxide of ethyle* is a white fusible solid.

The general formula of the neutral margarates is $C_{34} H_{33} O_3 MO$, or $C_{68} H_{66} O_6, 2 MO$. We cannot say with certainty whether margaric acid is unibasic, as the first of these formulæ would indicate, or bibasic, according to the second. We shall return to this point after describing stearic acid, and we shall also then describe the action of heat on both acids.

23. Stearic Acid. $C_{68} H_{66} O_5, 2HO = \overline{St}, 2HO$.

This is, perhaps, the most important and most abundant of the fatty acids. It exists, in combination with glycerine, as *stearine,* in beef and mutton fat, and in several vegetable fats, such as the butter of cacao. To obtain it, mutton suet is saponified by boiling with potash, and the purified soap decomposed by an acid, when a mixture of stearic and oleic acids, the latter in small proportion, rises to the surface. It is strongly pressed between warm plates, so as to get rid of the oleic acid in great part, and it is finally purified by solution in hot alcohol, and crystallisation, repeated till its melting point is constant at 167°. Or the stearic acid of commerce, which is nearly pure, may be purified by means of alcohol. Or again, tallow may be mixed with half its weight of oil of vitriol, and the mass melted in hot water, which removes a compound of sulphuric acid with glycerine, while the stearic acid rises to the surface and is to be purified as above. Finally, pure stearine, if saponified, and the soap acted on by an acid, yields at once pure stearic acid.

Stearic acid is a white solid, fusible at 167°, and on cooling forming brilliant white needles. It may be reduced to powder, and is, like all fat acids, insoluble in water, soluble in alcohol and ether. It burns like wax, and is used in the formation of improved candles.

By the action of nitric acid and other oxidising agents, stearic acid is at once converted into margaric acid, and it will be seen that the addition of 1 eq. oxygen is sufficient to effect this change. $C_{68} H_{66} O_5, 2 HO + O = C_{68} H_{66} O_6, 2 HO$.

Stearic acid is bibasic, and forms two series of salts; $St, 2 MO$, and St, MO, HO. The neutral stearates of the alkalies are perfect soaps. They dissolve in from 10 to 20 parts of hot water, and the addition of a large quantity of water decomposes them into acid stearates which are deposited, and basic stearates which remain dissolved. For the same reason a hot solution of a neutral stearate becomes gelatinous on cooling, from the separation of the acid salt. *Acid stearate of oxide of ethyle,* $St, Ae O, HO$, and *neutral stearate* of the same base, $St, 2 Ae O$, are both white crystalline fusible solids; as is likewise the *stearate of oxide of methyle,* $St, 2 Mt O$.

Stearine, the chief ingredient of suet and tallow, appears to be the *acid stearate of oxide of glyceryle,* but its precise formula cannot be determined as long as we are doubtful about that of glycerine. If glycerine be $C_3 H_2 O$, then stearine will be $C_{68} H_{66} O_5 + C_3 H_2 O + 2 HO = \overline{St}, Gly O, 2 HO$; but if stearine be $C_6 H_7 O_5$, the formula will be 2 $(C_{70} H_{67} O_5)$ + Gly O + 2 HO; (using the older formula for stearic acid). Neither of these formulæ is satisfactory, as both exhibit 3 eq. of base and basic water, instead of two or four. When boiled with alkalies, stearine, like all other fats, is saponified: that is, the stearic acid combines with the alkali, forming soap, and glycerine is separated. Pure stearine is obtained by pressing tallow between hot plates, and afterwards dissolving in hot ether, which on cooling deposits the stearine. It is like wax in appearance when it has been melted, and it may be powdered.

Stearate of lead is an insoluble fusible soap, or, as it is called, a plaster. The same is true of margarate of lead, and in general of the compounds of lead with fat acids.

The composition of stearic acid stands in a very simple relation to that of margaric acid. If we call the compound $C_{34} H_{33}$, *margaryle*, and view it as a compound radical, representing it by the symbol Ml, then $Ml\ O_5$ = stearic acid, and $Ml_2 O_6 = 2\ Ml\ O_3$ = margaric acid. These acids, therefore, bear to each other the same relation as that which subsists between sulphuric and hyposulphuric acids, $S O_3$ and $S_2 O_5$. The only difference is that, while $S O_3$ neutralises as much base as $S_3 O_5$, $Ml\ O_3$ only neutralises half the quantity of base neutralised by $Ml_3 O_5$, or in other words, $Ml_2 O_6$ neutralises as much base as $Ml_2 O_5$.

When stearic acid is distilled alone, or with lime, it yields much margaric acid, and a neutral fusible crystalline fat, margarone, besides a solid carbo-hydrogen $C_{34} H_{34}$, carbonic acid, and water. Margarone is either $C_{33} H_{33} O$, or $C_{34} H_{33} O$. In the former case it is formed from margaric acid by the loss of 1 eq. carbonic acid; in the latter, it is the oxide of the supposed radical margaryle, Ml O. The production of these compounds is easily understood, for 2 eq. stearic acid are equal to 3 eq. margaric acid and 1 eq. oxide of margaryle; $2\ Ml_2 O_5 = 3\ Ml\ O_3 + Ml\ O$. Again, 4 eq. of hydrated stearic acid contains the elements of 6 eq. hydrated margaric acid, 1 eq. margarone, $(C_{33} H_{33} O)$, 1 eq. water, 1 eq. carbonic acid, and 1 eq. of the carbo-hydrogen $C_{34} H_{34}$. It would appear that according to circumstances the margarone has a different composition, its properties varying little, so that different chemists have obtained different margarones: namely, $C_{33} H_{33} O$; $C_{34} H_{33} O$; and even $C_{68} H_{66} O = Ml_2 O$. When margaric acid is heated, part distils unchanged, and part is converted into the above products.

When margarine or stearine are distilled, they yield the very acrid vapours of acroleine, a product derived from the glycerine contained in these fats; but pure stearic and margaric acids yield not a trace of acroleine. Neither do they yield any sebacic acid among the products of their distillation, this acid being derived exclusively from oleic acid.

ACTION OF NITRIC ACID ON MARGARIC ACID.

By the action of nitric acid stearic acid is converted into margaric acid, with disengagement of nitrous acid vapours. But if the action of the nitric acid be prolonged, the margaric acid is gradually oxidised and dissolved, being converted into *suberic acid, succinic acid,* and an oil soluble in nitric acid.

24. Suberic Acid. $C_8 H_6 O_3, HO = \overline{Su}, HO$.

This acid is formed when cork is oxidised by nitric acid, but especially when nitric acid acts on stearic acid, margaric acid, oleic acid, and other fatty bodies. The acid solution, obtained by boiling stearic or margaric acid with nitric acid till it is entirely dissolved, is evaporated to one half, and on cooling deposits a large quantity of suberic acid, which is easily purified by crystallisation.

It forms small granular crystals, fusible, when moist, at 130°, when dried, at 248°, volatile at a higher temperature, and subliming in the form of long needles. It is sparingly soluble in cold water, very soluble in hot water, in alcohol, and ether.

The general formula of the suberates is Su, MO. The *suberate of oxide of ethyle* is prepared like the ethers of all the fatty acids, by passing hydrochloric acid gas through the alcoholic solution of the acid. When suberate of lime is distilled, it yields, among other oily products, a liquid boiling at 366°, the formula of which is $C_8 H_7 O$. It may be either the oxide of $C_8 H_7$, or the hyduret of $C_8 H_6 O$. It is converted into suberic acid by the action of the air and of nitric acid. In fact, the addition of 3 eq. of oxygen gives the composition of hydrated suberic acid, $C_8 H_7 O_4$. It is probable that there exists a radical *suberyle* $= C_8 H_6 O = Su$; and that we have $Su H$, and $Su O_2, H O$ for the oil and suberic acid, analogous to the hyduret of benzoyle and benzoic acid.

25. Succinic Acid. $C_4 H_2 O_3, HO = \overline{S}, HO$.

This acid exists ready formed in amber, and may be obtained by distilling that body. But the mother liquor of the suberic acid, formed from margaric acid, &c., by nitric acid, contains a large quantity of succinic acid, along with a little suberic acid. The mixture, being dried up, is acted on by ether, which dissolves the suberic acid, leaving the succinic acid ; it is finally purified by sublimation.

It forms regular crystals, which may be easily sublimed. The formula of the sublimed crystals is $2\,(C_4H_2O_3)+HO$; but by repeated sublimation it may be obtained anhydrous. The first hydrate $\overline{S}, HO$, melts at 356°, and boils at 455°, subliming, however, slowly at 284°. The sublimed hydrate, $2\,Su + HO$, melts at 320°, and boils at 468° ; and the anhydrous acid melts at 257°, and boils at 482°.

By the action of anhydrous sulphuric acid, it yields a new acid, apparently $C_8H_2S_2O_{10}, 4\,HO$, hyposulphosuccinic acid.

The constitution of the succinates is still doubtful ; but the most recent researches of Fehling, who has twice examined these salts with care, lead to the general formulæ of $C_4H_2O_3$, MO, for the neutral, and $2\,(C_4H_2O_4)+MO, HO$, for the acid salts. The *succinates of lead* present some anomalies. By the action of ammonia, NH_3, on succinic ether, $C_4H_2O_3, C_4H_5O$, there is formed succinamide, $C_4H_2O_2, NH_2$, while alcohol, C_4H_5O, HO is given off. When acid succinate of ammonia is heated, there is sublimed a new body, bisuccinamide, $C_8H_3O_4$, NH_2. It is formed from 2 eq. succinic acid and 1 eq. ammonia, by the separation of 2 eq. water. In their mode of formation these two bodies resemble oxamide and oxamic acid, only bisuccinamide has no acid properties.

The origin of *amber* is very uncertain ; but it is most probably derived from some resin, formerly liquid or soft. It may possibly have arisen from the slow oxidation of a fatty matter, as we see succinic acid formed from fats by oxidation. Amber is a clear brittle yellow solid, becoming electric by friction. It is for the most part insoluble in all menstrua. When heated, it yields succinic acid and a volatile oil, and there is left a large proportion of a matter which may be called bituminous, and forms the principal part of the amber.

26. Oleic Acid. $C_{36}H_{33}O_3, HO = \overline{Ol}, HO$.

This acid, in combination with glycerine, constitutes, as oleine, the liquid or most fusible portion of fats and fat oils. It exists in small proportion in tallow or suet ; more abundantly in human fat, hog's lard, and butter ; and it predominates in olive oil and especially in almond oil. To obtain it, almond oil is saponified, and the mixed fat acid obtained from the soap is digested with half its weight of oxide of lead, by which means margarate and acid oleate of lead are formed. Ether dissolves the latter only, and the ethereal solution of oleate of lead is acted on by hydrochloric acid, when the ether rises to the surface, holding the oleic acid in solution. The ether being distilled off, the oleic acid is left somewhat coloured, and it is purified by exposure to cold when the pure acid crystallises; or by converting it into oleate of baryta, which is purified by means of alcohol. When pure it is a nearly colourless oily fluid, freezing in cold weather. At temperatures above 57° it is a fluid oil, but when once melted, it does not solidify till cooled to 40°, and when solid, it does not melt till heated to 57°. It rapidly absorbs oxygen from the air and becomes brown.

It forms salts with bases, and the oleates of the alkalies are soaps. Naples soap is chiefly oleate of potash: oleate of soda is harder.

Nitric acid converts oleic acid into suberic acid and other products. By hyponitric (nitrous) acid or nitrate of mercury it is converted into *elaidic acid.*

When distilled, oleic acid gives rise to sebacic acid, and this is an infallible test of the presence of oleic acid or oleine in any fat. This character applies to all the varieties of oleic acid, although we have reason to think that the oleic acids of fat oils and of drying oils are very different. Indeed, according to recent researches, the oleic acid of linseed oil is $C_{46}H_{38}O_5, HO$.

Of the oleates, the most important are those of potash and soda, which exist in most soaps, and constitute the chief part of those made with olive or almond oil, or whale oil, and that of lead, which is a valuable ingredient of most plasters. *Oleate of oxide of glycerile,* as already mentioned, is *oleine,* the liquid part of fats and fat oils, which is hardly known in a perfectly pure state. Oleate of oxide of ethyle is an oily liquid.

27. Sebaic Acid. $C_{10}H_8O_3, HO = \overline{Sc}, HO$.

When any oil or fat, containing oleine or oleic acid, is distilled, and the product boiled with water, the hot filtered liquid deposits, on cooling, *sebacic acid* in small crystals resembling benzoic acid. It is soluble in alcohol and ether, and sublimes without alteration. The salts of sebacic acid are not remarkable, with the exception of the *sebate of oxide of ethyle,* which has a fragrant smell of melons. When we wish to ascertain the presence of oleine in a fat, a portion is distilled, the product is boiled with water, and the liquid, even if it deposit nothing, is tried by acetate of lead, with which it forms a white precipitate if sebacic acid be present.

28. Elaidic Acid. $C_{36}H_{33}O, HO$.

This acid is formed by the action of nitrous acid on oleic acid, with which it is isomeric. If a current of nitrous acid be passed through well-cooled oleic acid, the latter soon solidifies in large scales, which are *elaidic acid.* It is purified by solution in alcohol. It forms silvery scales, melting at 112°, very soluble in alcohol, and volatile without decomposition, except to a very small extent. The salts of this acid are soaps, and resemble those of the other fat acids.

Oleine is converted into *elaidine* (elaidate of glycerine), and oleic ether into elaidic ether, by the action of nitrous acid; but we cannot yet account for the production of elaidic acid in these cases or in that of its formation from oleic acid; since the mode of action of the nitrous acid is quite obscure.

ACTION OF NITRIC ACID ON OLEIC ACID.

When oleic acid is acted on by nitric acid, it yields several acids, only one of which, suberic acid, occurs in the action of nitric acid on other fat acids. The remaining acids are, *azelaic acid? pimelic acid, adipic acid, lipic acid,* and *azoleic acid,* all of which are crystallisable, besides no less than nine volatile acids, all belonging to the series $(CH)n+O_4$. (Redtenbacher).

The action of nitric acid on oleic acid is violent. When completed, the liquid is evaporated to one-half, and on cooling deposits suberic acid, which, according to Laurent, is accompanied by azelaic acid, very similar to it, the composition of which he describes as the same as that of suberic acid, or only differing by 1 eq. of water, while he gives the formula $C_{10}H_8O_4, HO$, that of suberic acid being $C_8H_6O_3, HO$. There is probably here an error of the press. But the existence of azelaic acid is very doubtful.

Pimelic acid crystallises on evaporation after the suberic acid has been removed, in hard granular crystals, fusible and volatile. Its formula is $C_7H_5O_3, HO$. In the mother liquid are found:—*Adipic acid* in round radiated masses, fusible and volatile. Formula $C_6H_4O_3, HO$ (Laurent), $C_{14}H_9O_7, 2HO$ (Bromeis), probably different acids. The *Lipic acid* forms long tables, very fine when formed in alcohol. Formula $C_5H_3O_4, HO$. *Azoleic acid,* according to Laurent, occurs in the form of an oily liquid, and œnanthic acid is also found. According to Bromeis, azoleic acid is doubtful, and the acid taken for it and for œnanthic acid is impure butyric acid, one of the oily acids observed in this reaction by Redtenbacher.

The volatile oily acids detected by that chemist are the following, being the first nine in the series so often mentioned, in which the hydrated acids have the formula $(CH)n+O_4$. We give them in a tabular form, with the empirical and rational formulæ:—

Acetic acid	$C_4\ H_4\ O_4 = C_4\ H_3\ O_3,\ HO.$
Metacetonic acid	$C_6\ H_6\ O_4 = C_6\ H_5\ O_3,\ HO.$
Butyric acid	$C_8\ H_8\ O_4 = C_8\ H_7\ O_3,\ HO.$
Valerianic acid	$C_{10}\ H_{10}\ O_4 = C_{10}\ H_9\ O_3,\ HO.$
Caproic acid	$C_{12}\ H_{12}\ O_4 = C_{12}\ H_{11}\ O_3,\ HO.$
Œnanthylic acid	$C_{14}\ H_{14}\ O_4 = C_{14}\ H_{13}\ O_3,\ HO.$
Caprylic acid	$C_{16}\ H_{16}\ O_4 = C_{16}\ H_{15}\ O_3,\ HO.$
Pelargonic acid	$C_{18}\ H_{18}\ O_4 = C_{18}\ H_{17}\ O_3,\ HO.$
Capric acid	$C_{20}\ H_{20}\ O_4 = C_{20}\ H_{19}\ O_3,\ HO.$

In this remarkable series of acids, each individual differs from the preceding by the addition of $C_2\ H_2$; and in like manner, the boiling point of each rises an equal number of degrees above that of the preceding one. The three or four highest in the series are even solid at ordinary temperatures, and it is probable that in all the melting point rises with the amount of $C_2\ H_2$, as regularly as the boiling point does.

The evident connection between all these acids is very interesting, as it accounts for their frequent occurrence in nature, more or less mixed together. Thus, in butter, which contains much oleic acid, we find four of these acids in small quantity, and it is remarkable that these four are not successive, but alternate in the series, the number of eqs. of carbon and hydrogen being in them divisible by 4. They are, butyric acid, C_8; caproic acid, C_{12}; caprylic acid, C_{16}; and capric acid, C_{20}. Redtenbacher observes, that the baryta salts of these four acids all form prisms, and that they are less soluble as the acid rises in the series; while the baryta salts of the intermediate acids, whose eqs. of carbon are divisible by 2, all crystallise in scales, and also diminish in solubility in ascending the scale. These curious facts furnish almost the only means of separating these acids from each other.

When oleic and elaidic acids are heated with potash there are produced acetic acid and a new fatty acid, $C_{32}\ H_{30}\ O_3$, HO. The difference between the formula of this acid and that of oleic acid is equal to 3 eq. acetic acid, which accounts for its production. Again, elaidic acid, $C_{72}\ H_{66}\ O_5$, *plus* 7 eq. oxygen, yields 2 eq. of the new acid, and 2 eq. acetic acid. This acid only differs from palmitic (ethalic) acid by 1 eq. hydrogen.

ACIDS OF CASTOR OIL.

Castor oil is a very peculiar oil. When saponified, it yields two fat acids, one crystallisable, *margaritic acid;* the other liquid, *ricinic acid.* The latter is little known. The former is said to be $C_{35} H_{31} O_6$. Castor oil is a mixture of the compounds of glycerine with these two acids. It is soluble, when pure, in its own bulk of alcohol. Nitrous acid converts it into a solid crystallisable fat, palmine, analogous to elaidine, but differing from it.

When castor oil is acted on by nitric acid, it yields a new volatile oily acid, of an agreeable aromatic odour, which is called *œnanthylic acid,* as its formula is that of œnanthic acid, *plus* 1 eq. oxygen ; $C_{14} H_{13} O_3$, HO. It forms an ether of a very agreeable aromatic smell. In the residue is found suberic acid.

Palmine, the fat formed by the action of nitrous acid on castor oil, is a white crystalline fat, which, when saponified, yields glycerine and a fatty acid, *palmic acid,* not yet fully investigated, but said by Playfair to belong to the series of margaryle, that is, to differ from margaric acid only in oxygen. A current of sulphurous acid passed though castor oil is said to produce palmine, or at all events a fat which yields palmic acid. This, if true, is a very singular fact, since nitrous acid, an oxidising agent, and sulphurous acid, a deoxidising one, would thus produce the same result.

NATURAL FATS AND FIXED OILS.

These are all compounds of glycerine with fatty acids. When heated with alkalies they yield soaps ; with oxide of lead, plasters; while in both cases glycerine is set free. The most common of all these compounds are stearine, margarine, and oleine, of which always two, and often all three, are present, stearine predominating in the hard, margarine in the soft, and oleine in the liquid fats. It is only the compounds of glycerine with volatile acids, such as butyric acid, that have a strong smell.

There are two kinds of fat oils : the fat oils proper, and the drying oils. The latter contain much oleine, the oleic acid of which is different from the usual oleic acid, and they absorb oxygen from the air, drying into a kind of varnish. When oils become rancid, they are partly decomposed ; and, generally, some of the acid, as well as of the glycerine, is set free, while oxygen is absorbed. Pure stearine, margarine, and oleine do not become rancid, and that change depends on a process of decay or slow oxidation going on in the impurities of the oil, and from them passing to the oil itself.

ACTION OF HEAT ON OILS AND FATS. ACROLEINE.

When oils are distilled they produce a variety of compounds, such as margaric acid, sebacic acid, margarone, carbohydrogens, &c. &c., and one most remarkable compound, *acroleine*, derived from glycerine.

Acroleine, $C_6 H_4 O_2$, is best obtained by distilling glycerine with phosphoric acid. The whole operation must be carried on in vessels full of carbonic acid gas, as the acroleine is very rapidly oxidised by the air. Its vapour attacks the eyes and nose in a most painful, indeed intolerable, degree. It may be considered as the hydrated oxide of a radical $C_6 H_3$, (*acryle*, analogous to acetyle) $C_6 H_3, O+HO$, analogous to aldehyde. It rapidly absorbs oxygen and forms *acrylic acid*, $C_6 H_3 O_3, HO$, analogous to acetic acid. In certain circumstances, the solution of acroleine exposed to the air deposits a white solid, $C_{10} H_7 O_4$.

The presence of acroleine among the products of the distillation of an oil or fat is a convincing proof of the presence of glycerine in that oil. It is worthy of remark that glycerine, $C_6 H_7 O_5$, is hydrated oxide of acryle, plus 3 eq. water, so that oils and fats may be called compounds of acroleine as well as of glycerine. It is even conceivable that acroleine may be $C_3 H_2 O$, which we have seen to be a probable form of glycerine in some fats; or that the glycerine in these fats may be acroleine, as above given, $C_6 H_4 O_2$, and that when this glycerine is separated by an alkali, it takes up 3 eq. of water.

Castor oil, so peculiar in other respects, exhibits a peculiar decomposition by heat. It yields acroleine, and a volatile oil, composed of two oils insoluble in alkalies; besides some saponifiable acids. When about one-fifth has been distilled, the residue suddenly consolidates into a spongy, yellow, elastic mass, insoluble in all menstrua except caustic alkalies, with which it forms peculiar soaps. These, when decomposed by an acid, yield a tough viscid substance having the characters of an acid. The product of the distillation again distilled with water, yields several oily compounds, one of which is crystalline, and not yet fully studied. The less volatile residue being again distilled yields a peculiar crystalline fatty acid, and another oily acid. Neither of these has been properly investigated.

When oils or fats are decomposed at a red heat, they yield much combustible gas (oil gas), formed of olefiant gas and marsh gas, and several liquid carbohydrogens: in particular benzole, $C_{12} H_6$, Faraday's quadricarboretted hydrogen, $C_4 H_4$, or $C_8 H_8$, and another isomeric compound, which is only liquid at very low temperatures.

ACTION OF SULPHURIC ACID ON FAT OILS.

Sulphuric acid, if added in small quantity to oils, combines with their glycerine; but if used in excess gives rise to a number of new products. In the first instance there are formed, when a mixture of oleine and margarine is acted on, two new acids, *sulpholeic acid* and *sulphomargaric* acid. These acids have not been isolated, but when their solution in water is heated, the sulphuric acid separates, and the oleic and margaric acids are transformed into four new acids, *metamargaric* and *hydromargaritic* acids, and *metoleic* and *hydroleic acids.* The two former are solid, crystallisable, and partly volatile. A compound of the two exists, which acts like a single acid and has been called *hydromargaric acid;* it is also a fusible solid. The two latter are oily, and all five appear to be bibasic. Their composition cannot be considered as ascertained, but the three first are nearly allied to margaric acid. It would lead to confusion here to mention the different formulæ proposed by Frémy, Berzelius, and Liebig, for these acids, more especially when it is considered that we have no sufficient evidence of the perfect freedom from foreign admixture of the acids analysed, and that the recent observations of Miller show an amount of variation in the melting points which leads to the suspicion of impurity. The subject is interesting, but difficult, and requires a very minute investigation.

Metoleic and hydroleic acids, when distilled, yield water, carbonic acid, and two carbohydrogens, *oleéne* and *elaéne*, both of which contain carbon and hydrogen in an equal number of equivalents; oleéne is supposed to be $C_{40} H_{40}$, and elaéne, $C_{15} H_{45}$; but this is not established.

ACTION OF NITROUS ACID ON FAT OILS.

Nitrous acid, or solution of nitrate of mercury, as already mentioned, causes fat oils to become solid, converting oleine into elaidine. This curious change takes place in olive oil, almond oil, rape-seed oil, hazel-nut oil, castor oil and others: but the drying oils, such as oils of linseed, hemp-seed, walnut, poppy-seed, &c., are not at all affected by nitrous acid. In all the oils which are changed into elaidine, except in castor oil, the product is the same. It is the formation of this solid fat which causes the mercurial ointments, made with nitrate, to become hard when kept. The elaidine, when purified by pressure and crystallisation in alcohol and ether, yields neither margaric nor oleic acid when saponified, but only elaidic acid, isomeric with oleic acid. There is probably a secondary reaction, for a red colouring matter is also formed, which has not been investigated.

Castor oil, as has been already mentioned, yields, with nitrous acid, a new fat *palmine*, which contains a new acid, *palmic* acid. These resemble elaidine and elaidic acid, but are quite distinct.

ACTION OF BASES ON FAT OILS. SOAPS AND PLASTERS.

When fat oils are boiled with solution of caustic alkalies, they are gradually dissolved in the water, if there be not too great an excess of alkali present, forming ropy or gelatinous solutions, which gelatinise on cooling. These are solutions of soaps, that is, potash and soda salts of the fatty acids, along with the glycerine set free. In order to have the soaps in a solid form, the solutions are boiled down, and when the alkali reaches a certain concentration, the soap becomes insoluble, and rises to the surface in a soft, half melted state. This is drawn off into moulds, and the mass formed on cooling is soap. Another method of causing the soap to separate from the water in which it is dissolved, consists in adding sea-salt, which at once coagulates the soap, converting it into a soap of soda, if it is a soap of potash. Of course, the glycerine, in both cases, is carried off in the mother liquid. Such is the theory of soap-making, which is very simple, depending on the affinity between the alkalies and the fat acids; on the solubility in water of the alkaline stearates, margarates, oleates, palmitates, &c.; and, finally, on the power of a certain amount of free alkali or of sea-salt to coagulate the soap and render it insoluble in the liquid in which it swims, and which in fact runs off its surface as water does off the surface of fat, while yet the soap retains perfectly its solubility in pure water.

The soaps of lime, baryta, &c., are insoluble in water, and have no detergent power: hence the waste occasioned by using hard, that is, calcareous, water for washing. All the salts of lime in such water must first be entirely precipitated in the form of curdy flocculi before any soap can be dissolved so as to act as a detergent.

The soaps of potash are soft, compared with those of soda, which are called hard soaps. White soap is stearate with some oleate, of soda. Naples soap is oleate and margarate of potash. Common soft soap is chiefly oleate of potash, but as it is made from whale oil or seal oil, it contains also phocenate of potash, which gives it a disagreeable smell.

Castile soap is oleate and margarate of soda, coloured by metallic oxides, chiefly oxides of iron, in such a way as to give the desired mottled appearance. Much and excellent soap is now made of palm oil, and is, therefore, palmitate of soda.

Soaps are soluble in alcohol, forming tincture of soap, which is an admirable liniment for bruises, and is much used along with laudanum, as tincture of soap and opium ; also with camphorated spirit, forming opodeldoc.

Plasters are soaps of certain metallic oxides, chiefly oxide of lead, which are insoluble in water, but fusible, and possess useful properties. Litharge plaster is made by boiling finely 5 parts of powdered oxide of lead with 9 parts of olive oil and some water, till the combination is complete. It is plastic at ordinary temperatures, and melts when heated. When solution of acetate of lead is added to solution of soap, plaster, that is, oleate and margarate of lead, is precipitated. When prepared in this way it becomes hard. White lead plaster, made with carbonate of lead, is very plastic and fusible, and is much used. Iron plaster and mercurial plaster are of small importance.

The chief liquid fat oils and drying oils of the vegetable kingdom have already been mentioned. In the animal kingdom, there are fish oils, characterised by containing phocenine ; also cod liver oil, &c. &c.

The solid oils or fats of the vegetable kingdom are, butter of cacao (*Theobroma cacao*); of nutmeg (*Myristica moschata*); of cocoa-nut (*Cocos nucifera*); of laurel (*Laurus nobilis*); palm-oil (*Avoira elais: Elais Guianensis*); galam butter (*Bassia butyracea*); and some others. Those of the animal kingdom are tallow, or suet, butter, hog's lard, human fat, &c.

Spermaceti is a peculiar fat found in the head of *Physeter macrocephalus.* When purified from a small quantity of a liquid oil, it constitutes *cetine*, which is a compound of ethal (hydrated oxide of cetyle) with cetylic acid, or at least yields those compounds when boiled with potash. Cetine crystallises beautifully when melted or when dissolved in hot alcohol. Cetine, when acted on by nitric acid, yields first pimelic acid, $C_7 H_6 O_4$; which is then oxidised into adipic acid, $C_{14} H_{12}$

O_{10}. Thus 2 $(C_7 H_6 O_4) + O_4 = C_{14} H_{12} O_{10}$. The adipic acid is finally converted into succinic acid; thus, 2 $(C_{14} H_{12} O_{10}) + O_{11} = 7 (C_4 H_3 O_4) + 3 HO$.

Cholesterine is a fat found in bile, and also, in small proportion, in the blood, and in much larger quantity as an ingredient of cerebral matter. It forms the chief ingredient of biliary calculi. It dissolves in hot alcohol, crystallises on cooling, in silvery scales, but cannot be saponified by boiling with potash. Its formula is either $C_{38} H_{33} O$, or $C_{36} H_{32} O$. When acted on by nitric acid, it yields a new acid, *cholesteric acid,* which contains nitrogen, probably as nitrous acid.

Ambreine, a fat analogous to cholesterine, is found in ambergris. It yields, with nitric acid, *ambreic acid.* Castorine is a similar fat found in castoreum.

Wax is another peculiar fatty body, the origin of which is derived from flowers, whence it is collected by the bee. It melts at about 150°. It is a mixture of two fats, *cerine* and *myricine,* the former soluble, the latter insoluble, in hot alcohol. Cerine is partly saponified by boiling with potash, yielding apparently margaric and oleic acids (?) along with a neutral fat, *ceraine* having the same composition as myricine. There are several kinds of vegetable wax, but they are all much more easily saponified than bees-wax. When bees-wax is distilled, it yields neither acroleine nor sebacic acid, and would therefore appear to contain neither oleic acid nor glycerine. When heated with nitric acid, wax is almost entirely converted into succinic acid.

Japan, or tree wax, is a true fat, composed of palmitic acid and glycerine without oleine. When acted on by nitric acid it yields first pimelic and adipic acids, and then succinic acid, as in the case of spermaceti.

Cerosine is the name given to a waxy substance occasionally found on the surface of the sugar-cane. It is not saponifiable, and appears to contain $C_{48} H_{50} O_2$.

Athamantine, from the root of *Athamanta oreoselinum,* is a crystalline fat-like body, containing valerianic acid, united to a body, *oreoselone,* which supplies the place of glycerine in the neutral athamantine. Oreoselone is $C_{14} H_5 O_3$, that is, isomeric with dry benzoic acid. Athamantine is $C_{24} H_{15} O_7 = C_{14} H_5 O_3$ (1 eq. oreoselone) $+ C_{10} H_{10} O_4$ (1 eq. valerianic acid. Athamantine combines with hydrochloric acid, and the compound, when boiled with water, deposits crystals, which are oreoselone *plus* water $= C_{14} H_6 O_4$, and isomeric with crystallised benzoic acid.

Having now briefly described the best known organic acids, it is necessary to mention a number of acids, found in the analyses of different vegetables, but not yet sufficiently studied to decide whether they exist independently, or may not rather be, in many cases, identical with some of the acids above described. Such are chelidonic acid, lately shown by Lerch to be analogous to meconic acid, and to have the formula $C_{14} H_5 O_{13} = C_{14} H_2 O_{10}, 3 HO$; caincic, crameric, caffeic, boletic, fungic, tanacetic, lactucic, atropic, cocognidic, solanic, coneic, aceric, moroxylic, kinovic, and menispermic acids, besides others.

VOLATILE OR ESSENTIAL OILS.

These oils are so called because they are obtained by distillation of vegetables, generally along with water, and because, having, in most cases, the concentrated odour of the plant, they are usually called essences. Most of them exist ready-formed in the plant, which owes its smell to them: but some, as oil of bitter almonds and oil of spiræa, are formed by a kind of fermentation, excited in the case of the former, as already stated, by the contact of amygdaline, emulsine and water.

Many plants, when cut, yield balsams, which are mixtures of essential oils and resins. In many essential oils a crystalline matter is deposited, called a camphor or stearoptene. They are all soluble in alcohol. Many absorb oxygen from the air and become acid, as oil of cinnamon. They are violently acted on by nitric acid and iodine, chlorine, bromine, &c.

They may be divided into three kinds: 1st, those containing only carbon and hydrogen, as oil of turpentine; 2nd, those containing also oxygen, as oil of cloves; 3rd, those containing sulphur, as oil of garlic.

1. Non-Oxygenated Essential Oils.

Almost every one of these (which constitute a very numerous class of oils), as yet accurately analysed, has been found to contain carbon and hydrogen in the proportion $C_{10} H_8$, or what is the same thing, $C_5 H_4$, or $C_{20} H_{16}$. The following are the most important.

Oil of turpentine, $C_{10} H_8$, or $C_{20} H_{16}$, is obtained by distilling, with water, turpentine, the juice exuding from many species of *pinus*. Rosin, resin, or colophonium, remains in the retort. The oil has a peculiar smell, and burns with a smoky flame. Its Sp. G. is 0·86. It boils at 312°. Strong nitric acid sets fire to it, and it is also decomposed with flame by chlorine. It dissolves sulphur, phosphorus, and fat oils. When exposed to hydrochloric acid gas, it combines with it, forming a white crystalline solid like camphor, and a liquid compound. The solid is $C_{20}H_{17}Cl = C_{20}H_{16}, HCl$. When heated with lime, it yields a pure oil, *dadyle*, $C_{20}H_{16}$. The liquid hydrochlorate, heated with lime, yields another pure oil, *peucyle*, rather more volatile than dadyle, but having the same composition. Oil of turpentine would seem to be composed of peucyle and dadyle, both $C_{20}H_{16}$; the former giving a liquid, the latter a solid compound, with hydrochloric acid.

Nitric acid, by long boiling, converts oil of turpentine into an acid, turpentinic acid, $C_{14}H_9O_7, HO$?

Oil of turpentine is used in medicine, internally, as a vermifuge, especially in cases of the larger worms, such as *tænia;* externally, as an excellent rubefacient and counter-irritant. In the arts it is much prized as a solvent for resins in making varnishes.

Oil of juniper has the same composition as oil of turpentine, but possesses its own peculiar odour, which it communicates to alcohol in *gin*. This oil is diuretic.

Oil of savine has the same composition. It is also diuretic. *Oil of elemi* has the same composition, and a pleasant odour. *Oil of storax*, or *styrole*, appears to have the composition of C_2H, or some multiple of it. Nitric acid acts on it, producing hydrocyanic acid, benzoic acid, and a fragrant crystalline body, nitrostyrole. Styrole itself is a very remarkable substance, differing as it does from all the other non-oxygenated oils. Dr. Blyth has been for some time engaged in its investigation, and has obtained very interesting results, not yet ready for publication.

Oil of lemons has the probable composition, C_5H_4. Like oil of turpentine it is composed of two isomeric oils, *citrene* and *citrylene*, which combine with hydrochloric acid, forming a liquid and a solid compound, decomposed by heating with lime. The solid camphor seems to be, $C_{10}H_9Cl = C_{10}H_8$, HLl. The oils of *cedro, cedrat, oranges, and limes*, are all essentially identical with oil of lemons. *Oil of neroli*, or of *orange-flower*, is quite distinct, having the odour of the flower, while the others have that of the rind of the fruit. Its composition is not accurately known.

Oil of copaiva is another isomeric form of oil of turpentine, which it very much resembles, forming a camphor with hydrochloric acid. It is diuretic, and much used in affections of the bladder and urethra. *Oils of pepper* and *of cubebs* are still of the same composition in 100 parts, although the latter is supposed to be $C_{15}H_{12}$.

2. Oxygenated Essential Oils.

The principal oils of this class have been already considered, their radicals being known. These are *oil of bitter almonds*, or hyduret of benzoyle ; *oil of spiræa*, or hyduret of salicyle ; *oil of cinnamon*, or hyduret of cinnamyle ; *oil of cloves* (eugenic acid) ; *oil of cumine*, or hyduret of cumyle ; *oil of aniseed*, the solid part of which is $C_{20}H_{12}O_2$, and with nitric acid yields anisic acid, and other compounds already described at p. 466 ; *oil of valerian*, chiefly valerianic acid, &c. The essence of valerian, according to Gerhardt, generally contains several compounds, especially if old. When fresh, it contains no valerianic acid, but an oil, *valerole*, which is crystallisable, and soon passes into valerianic acid in the air. This oil is $C_{12}H_{10}O_2$, and is isomeric with metacetone, also with Kane's oxide of mesityle, and with oxide of allyle (see oil of garlic, p. 490). Besides valerole, the essence contains a carbo-hydrogen, *bornéne*, $C_{10}H_8$, identical with the oil obtained from borneo camphor ; and finally, a camphor, which is identical with borneo camphor.

Oil of cinnamon, according to Mulder, is, when quite fresh, $C_{20}H_{11}O_2$. It rapidly attracts oxygen, and $3(C_{20}H_{11}O_2) + O_8 =$ 1 eq. cinnamic acid, 1 eq. resin alpha, $C_{12}H_5O$, 1 eq. resin beta, $C_{30}H_{15}O_4$, and 6 eq. water H_6O_6. With hydrochloric acid it yields two different resins, $C_{20}H_8O$, and $C_{14}H_7O$, besides other products. With oil of vitriol it yields two more resins, $C_{30}H_{15}O_2$, and $C_{30}H_{15}O$, which together are equal to 3 eq. of the oil *minus* 3 eq. water. With nitric acid the fresh oil forms a crystalline compound, $C_{18}H_9NO_7 = C_{18}H_8O_3 + NO_3 + HO$. With water this body yields hyduret of cinnamyle, $C_{18}H_8O_2$. If dissolved in sulphuric acid and mixed with water it gives cinnamic acid, $C_{18}H_7O_3$. Along with the crystals, nitric acid yields a red oil, which, with water, gives another oil, $C_{15}H_7O_2$.

Oil of anise, $C_{20}H_{12}O_2$, yields with bromine a compound in fine crystals, $C_{20}\left\{\begin{matrix}H_9\\Cl_3\end{matrix}\right.O_2$. When acted on by strong acids, or by the chlorides of tin or antimony, oil of anise is converted into an isomeric body, anisone, analogous to benzoine.

Of the remaining oils of this class may be mentioned the oils of *dill*, of *fennel*, of *parsley*, of *carraway*, of *coriander*, of *pim-*

pernel, of *peppermint* ($C_{10} H_{10} O$, or $C_{20} H_{20} O_2$; this oil yields several new compounds with chlorine), of *marjoram*, of *lavender*, *rosemary*, *basil*, *thyme*, *rue* ($C_{28} H_{28} O_3$), *cascarilla*, *chamomile*, *wormwood*, *tea*, *cardamom*, *nutmeg*, *cajeput*, *rhodium*, *rose* (otto or attar of roses), *bergamot*, *saffron*, *sassafras*, and *sweet bay* ($C_{20} H_{16} O$). Of these, little certain is known, and almost all require a careful study. The oil of sassafras, $C_{10} H_5 O_2$, when cooled, deposits very large and beautiful crystals, measuring 1½ inch on the side. With bromine, the solid essence yields crystals, composed of $C_{10} H Br_4 O_2$.

The oil or essence of *semen contra* is said to be $C_{18} H_{15} O_2$. That of *artemisia dracunculus*, or essence of estragon, yields, when treated with sulphuric acid, *anisoine*, identical with that of oil of anise, and in fact contains the same oxygenated oil (stearoptene of anise), along with a different carbohydrogen. Laurent has obtained from essence of estragon a series of new compounds. He represents the essence by $C_{32} H_{20} O_3$; but Gerhardt has shown that it is identical with the oil of anise, and that draconic acid and dracole are the same as anisic acid and anisole. The acid is $C_{14} H_7 O_5, HO$.

The concrete essence of the tonka bean is called *coumarine*. It is very fragrant, and its formula is $C_{18} H_6 O_4$. Potash changes it first into cumaric acid, $C_{18} H_7 O_5, HO$, and afterwards into salicylic acid; and hot nitric acid converts it into nitropicric acid. Cold nitric acid produces a white volatile crystalline solid, $C_{18} \left\{ \begin{matrix} H_5 \\ NO_4 \end{matrix} \right. O_4$. Coumarine also combines with chloride of antimony, forming yellow crystals.

3. Sulphuretted Essential Oils.

This class of oils is distinguished by a pungent peculiar smell, and acrid burning taste, as in oil of mustard, or an intense alliaceous odour, as in oil of garlic or of onions. The more important of them have been lately investigated, and have yielded very striking results.

Essence of mustard is prepared from mustard-seed in the same way as oil of bitter almonds from that seed. The seed is macerated with water and afterwards distilled, when it yields an oil of a most remarkable nature, containing not only sulphur, but also nitrogen. The pure oil is colourless, of Sp. G. 1·010, and boils at 298° or 300°. Its formula is $C_8 H_5 N S_2$, so that it contains no oxygen. With ammonia it forms a crystalline compound, which is, in fact, an organic base or alkali, *Thiosinnamine* $= C_8 H_8 N_2 S_2$. This is a bitter compound, which forms, like nearly all organic bases, crystalline compounds with chloride of platinum and chloride of mercury.

Thiosinnamine, acted on by dry oxide of lead or of mercury, loses all its sulphur, forming a new base, *sinnamine* $= C_8 H_6 N_2 = C_8 H_8 N_2 S_2 - 2 HS$. It is, therefore, Thiosinnamine, minus 2 eq. sulphuretted hydrogen, which have acted on the oxide of lead, forming water and sulphuret of lead. Sinnamine forms definite compounds with chlorides of mercury and platinum. It is a powerful base, and very bitter to the taste.

When oil of mustard is acted on by moist hydrated oxide of lead, it loses both sulphur and carbon, in the proportion CS_2, forming sulphuret of lead and carbonate of lead, along with a new base, *sinapoline*, which dissolves in hot water, in alcohol, and in ether. Its formula is $C_{14} H_{12} N_2 O_2$; and it is formed from 2 eq. oil of mustard, with 6 eq. oxide of lead and 2 eq. water, as follows: $2 (C_8 H_5 NS_2) + 6 PbO + 2 HO = C_{14} H_{12} N_2 O_2 + 4 PbS + 2 (PbO, CO_2)$.

When oil of mustard is acted on by an alcoholic solution of potash, there is separated neutral carbonate of potash, and the addition of water causes the separation of an oily liquid, which is in its relations analogous to oil of mustard. It appears to be $C_{28} H_{25} N_3 S_4 O_4$. By the action of baryta upon it, sulphuret of barium is formed, and a basic compound not further examined. The liquid from which this oil has separated contains the potassium salt of a very remarkable acid, which forms with a salt of lead the compound $C_8 N H_6 S_4, Pb, = C_8 H_5 NS_3, HS + PbS$. These compounds are produced as follows: 6 eq. oil of mustard, 10 of water, and 2 eq. of potash, $6 (C_8 H_5 NS_2) + 10 HO + 2 KO$, yield 1 eq. of the new oil $C_{28} H_{25} N_3 S_4 O_4$, 1 eq. ammonia NH_3, 4 eq. carbonic acid, $C_4 O_8$, and 2 of the new salt of potassium $2 (C_8 H_6 NS_4, K)$. It is probable, however, that the first change is more simple, and that 3 eq. oil of mustard, 5 of water, and 1 of potash, yield 1 eq. of an oil $C_{14} H_{14} N_2 S_2 O_2$, 2 eq. carbonic acid, $C_2 O_4$, and 1 of the potassium salt $C_8 H_6 NS_4, K$. Two eq. of the oil $C_{14} H_{14} N_2 S_2 O_2$ lose 1 eq. ammonia, and give rise to the oil $C_{28} H_{25} N_3 S_4 O_4$.

These very interesting facts, important in a high degree from their bearing on the theory of organic bases, are taken from a paper by Dr. Will lately published, to which I refer the reader. Dr. Will points out some curious relations. Thus sinapoline, $C_{14} H_{12} N_2 O_2$, may be derived from 2 eq. oil of mustard and 6 eq. water, which yield 1 eq. sinapoline, 2 eq. carbonic acid, and 4 eq. sulphuretted hydrogen. If we now suppose 2 of the 4 eq. of HS to combine with 1 eq. sinapoline, they will produce the oil, $C_{14}H_{14}N_2O_2S_2$, which is supposed to be first formed and afterwards to lose ammonia: while, if the 2 other eqs. of HS combine with 1 eq. of unchanged oil of mustard they will form the acid of the new potassium salt: $C_8H_5NS_2 + 2HS = C_8H_7NS_4$.

Again, sinapoline may be viewed as hyduret of benzoyle, *plus* 2 eq. ammonia, $C_{14}H_6O_2, 2NH_3$; and the hypothetical oil is then $C_{14}H_6O_2, N_2H_8S_2$, or hyduret of benzoyle, *plus* 2 eq. sulphuret of ammonium.

The separation of the elements of bisulphuret of carbon from oil of mustard, and the simultaneous formation of a series of basic compounds, would indicate that oil of mustard might be a compound of sulphocyanogen; since sulphocyanide of ammonium, when heated, gives off bisulphuret of carbon, and gives rise to a series of basic compounds, melamine, ammeline, &c. Now it is very remarkable that oil of mustard admits of being considered as $C_6H_5 + C_2NS_2$, that is the sulphocyanide of a new radical *allyle*, C_6H_5; of which, as we shall presently see, oil of garlic is the sulphuret. Finally, oil of mustard may be a compound of hydrocyanic acid with the hydrosulphuret of sulphuret of acryle: $C_6H_3S, HS + C_2NH$. Its very pungent smell and powerful action on the eyes certainly rank it beside acroleine, C_6H_3O, HO. The researches of Wertheim have lately demonstrated the truth of the supposition above mentioned, and the oil of mustard, or sulphocyanide of allyle, has been formed artificially from the oil of garlic, the sulphuret of allyle, and *vice versâ*.

Oil of mustard contains an indifferent nitrogenised body, *myrosine*, which, analogous to emulsine, yields the essential oil after maceration of the seed with water, and fermentation. The fermentation of myrosine is prevented in the same way as that of emulsine, namely by coagulation. The seeds also contain a crystalline body, *sinapisine*, resembling a fat. The substance, which, along with myrosine, yields the oil, appears to be *myronic acid*, or rather *myronate of potash*, a body not yet fully studied. The seeds of *Sinapis alba* contain the myrosine, as sweet almonds contain emulsine; but, being destitute of myronic acid or myronate of potash, as sweet almonds are of amygdaline, they yield none of the oil.

It has very recently been shown by Hubatka and Wertheim, that the essential oils of *Cochlearia armoracia* (horse-radish), *Cochlearia officinalis*, and *Alliaria officinalis*, consist almost entirely of oil of mustard, although the latter oil has also a very strong smell of oil of garlic, an oil which has not been discovered in it.

The essential oil of garlic, from the bulbs of *Allium sativum,* is a peculiar sulphurised compound. Wertheim has lately studied it, and shown that it is the sulphuret of a new radical Allyle $= C_6 H_5 =$ All, and its formula is $C_6 H_5, S =$ AllS. The crude oil contains a little of a higher sulphuret, possibly $AllS_2$, and also some of the oxide of allyle, $C_6 H_5 O =$ All O, which is an oily liquid of an offensive smell. The radical allyle appears to enter into numerous combinations, and, among others, Wertheim analysed the following: the sulphuret, or pure oil of garlic, AllS; the compounds of that sulphuret with the sulphurets of platinum, palladium, and silver, $5\,AllS + 6\,PtS_2$: $2\,AllS + 3\,PtS_2$; $2\,AllS + 3\,PdS$; and $x\,AllS + AgS$?; double compounds with the sulphurets and chlorides of mercury and platinum; $3\,(AllS + PtS_2) + (AllCl + PtCl_2)$; and $(AllS + 2\,HgS) + (AllCl + 2\,HgCl)$; and lastly nitrate of the oxides of silver and allyle, $(AllO + AgO) + NO_5$. Our space does not permit us to do more than point out the existence of these curious compounds.

The essential oil of *assafetida* appears to consist of at least two oils, one of which, if not both, contains sulphur. It has a very offensive odour. It does not combine with ammonia like the oil of mustard. Dr. Douglas Maclagan finds, as might be expected from the odour, that one of the oils it contains is sulphuret of allyle.

The essential oils of *hops,* of *water pepper,* and of *Arum maculatum,* are believed to contain sulphur.

CONCRETE VOLATILE PRINCIPLES, ALLIED TO THE ESSENTIAL OILS.

There are several substances which may be classed under this head; such as *Hellenine* from *Inula helenium,* which is a volatile crystalline solid, $C_{15} H_{10} O_2$. With nitric acid it yields *nitrohellenine* $C_{15} \left\{ \begin{matrix} H_9 \\ NO_4 \end{matrix} \right. O_2$. When distilled with anhydrous phosphoric acid, hellenine loses 2 eq. water, yielding *hellenéne,* a carbohydrogen, $C_{15} H_8$. With chlorine it yields the compound $C_{15} \left\{ \begin{matrix} H_9 \\ Cl \end{matrix} \right. O_2 + HCl$.

Asarone from *Asarum europæum* is a volatile solid, having a remarkable tendency to crystallise in beautifully defined forms, and also to pass into the amorphous condition, from which it may be again brought into the crystalline state. Schmidt has very recently studied its crystallisation under the microscope, and has obtained results which are most interesting in reference to the formation of crystals in general. I must refer to his elaborate paper in the "Annalen der Chemie und Pharmacie," for February 1845. Its composition is, $C_{20} H_{13} O_5$.

Anemonine, from various species of *Anemone,* is a volatile, crystallisable solid, the formula of which is $C_5 H_2 O_2$. It forms with oxide of lead a compound, $3 (C_5 H_2 O_2) + PbO$. With bases it yields *anemonic acid,* the composition of which is unknown.

Cantharidine, the active principle of Spanish flies, is a volatile acrid solid, the composition of which is $C_{10} H_6 O_4$.

The following plants, *Epidendron vanilla, Quassia amara, Tanghinia madagascariensis, Primula auricula,* and *Primula veris,* contain concrete volatile essences, not yet analysed.

CAOUTCHOUC, OR GUM ELASTIC.

Caoutchouc is a substance *sui generis,* which in composition approaches more nearly to the essential oils than to any other class of compounds. It is the coagulated or inspissated juice of many tropical trees, the chief of which is *Siphonia elastica* (*Iatropha elastica, Hevea guianensis*). The juice, as it flows from the tree, is made to dry on moulds of clay, which are afterwards broken out, leaving a bottle of caoutchouc. It is generally blackened by smoke, but when pure it is white and transparent, it is highly elastic, and the freshly cut surfaces adhere strongly if pressed together. It is insoluble in water, alcohol, and acids: but it dissolves in ether, naphtha, coal-tar naptha, bisulphuret of carbon, and essential oils. Its solutions in ether and coal-tar naphtha, when dried up, leave the caoutchouc in an elastic state. On this principle waterproof cloth is made. Caoutchouc is much used in chemical operations to form flexible connecting tubes.

When exposed to heat, caoutchouc first melts, and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbohydrogens. Some of these oils boil at 90°, others at 680°, and at intermediate points. I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, when acted on by sulphuric acid, yielded an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, $C_5 H_4$ or $C_{10} H_8$. One of these, called *caoutchine,* gives with chlorine an oil, $C_{10} H_8 + Cl$.

RESINS.

Resins are generally found along with essential oils, and many of these oils, by the action of the air, are converted into resins. In this change, the essential oils lose a part of their hydrogen, which is converted into water, and take up some oxygen besides. In fact, the resins, as a class, are acid bodies. They are insoluble in water, but become soft in boiling water. They dissolve in alcohol, and often crystallise from that solvent.

The acid resins combine with bases; their salts with the alkalies are called resinous soaps. The resins are not volatile, although very inflammable. They are purified from essential oils by distilling off the latter along with water; but, as thus obtained, they are generally mixtures of several resins.

Turpentine and *Colophony*, or *Common Resin.* Turpentine is the semifluid juice which exudes from many species of *Pinus.* When distilled with water, it yields oil of turpentine, $C_{10}H_8$ or $C_{40}H_{32}$, while colophony or resin remains behind, which is $C_{10}H_7O$, or $C_{40}H_{28}O_4$, or, more accurately, $C_{40}H_{30}O_4$. Here the oil, $C_{40}H_{32}$, has lost 2 eq. hydrogen, replaced by 2 eq. oxygen, $C_{40}H_{30}O_2$, and this compound, like aldehyde, has taken up 2 eq. of oxygen to form the acid resin, $C_{40}H_{30}O_4$.

Colophony contains two different resins: resin *alpha*, or *pinic acid*, and resin *beta*, or *sylvic acid.* The latter is said to be $C_{20}H_{15}O_2$, the former isomeric with it, $C_{40}H_{30}O_4$; and their properties are very similar, being those of colophony which is formed of them. The sylvic acid is crystallisable.

When distilled with lime, colophony yields two oily liquids, *resineone*, $C_{26}H_{23}O$, and *resinone*, $C_{10}H_9O$.

The *resin of copaiva* is $C_{40}H_{30}O_4$, according to Rose; but there is some reason to believe that it is isomeric with the preceding. A variety of it has occurred, containing $C_{40}H_{34}O_8$, and when combined with oxide of lead, $C_{40}H_{28}O_6$. This resin crystallises.

The *resin of elemi* contains two resins, one crystallisable. Both are said to be $C_{20}H_{16}O_2$. *Anime* also contains two resins. *Euphorbium* yields a resin having the same composition as elemi. *Benzoin* contains, besides benzoic acid and a volatile oil, three resins, *alpha*, $C_{70}H_{42}O_{14}$; *beta*, $C_{40}H_{22}O_9$; and *gamma*, $C_{30}H_{20}O_5$. The resin alpha contains the sum of the other two, and by long boiling with carbonate of soda, which dissolves the resin gamma alone, is resolved into them.

Balsam of Tolu contains, besides essential oil, benzoic and cinnamic acids, and a carbohydrogen, $C_{24}H_{18}$, a resin, $C_{18}H_{10}O_5$. It contains the elements of benzoic ether, *plus* 1 eq. oxygen. When the balsam is distilled, *per se*, it actually yields benzoic ether, along with a new carbo-hydrogen, called benzoéne, or *toluole*, $C_{14}H_8$. This last compound yields with sulphuric acid a new acid $C_{14}H_7S_2O_5 + 3\,HO$; and, with nitric acid, two new nitrogenised compounds, $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right.$, called *protoni-*

trobenzoéne, or *nitrotoluide*, analogous to nitrobenzide, and another, binitrobenzoéne, $C_{14} H_6 + 2 N O_4$. The former is isomeric with salicylamide, and with anthranilic acid, and, like the latter body, when heated with lime, yields aniline. When acted on by hydrosulphuret of ammonia, it yields another artificial base, toluidine. With chlorine, benzoéne also yields several new products.

Styracine, the resin of styrax, is $C_{24} H_{11} O_2$. When acted on by nitric acid, it yields the products of decomposition of cinnamic acid. When fluid storax is distilled with water, it yields a remarkable oil, *styrole*, $C_{16} H_8$, which is also formed by the action of heat on cinnamic acid, and is probably derived from cinnamic acid present in the storax.

Styrole, when heated to 400° in a closed tube, changes into a solid glassy mass of the same composition in 100 parts, but the formula of which is $C_{14} H_7$. It is called *metastyrole*. By a stronger heat, it is volatilised and reconverted into the oil. Styrole is analogous to benzole and toluole, and like them, forms compounds, when acted on by nitric acid, in which H is replaced by NO_4 (Hoffmann and Blyth).

The resin of guaiacum is remarkable for its tendency to become blue by the contact of many different substances. It contains two resins, but their composition is not ascertained. *Lac* contains four resins, besides colouring matter. *Dammara*, *mastic*, *dragon's blood*, and *sandarach*, are resins much used in making varnishes.

Jalap contains two resins; one, a soft resin soluble in ether, $C_{42} H_{34} O_{18}$; and an acid resin insoluble in ether, which, from striking a fine red colour with sulphuric acid, is called *rhodeoretine*, $C_{42} H_{35} O_{20}$. When combined with bases, it takes up 1 eq. water, forming *hydrorhodeoretine*, very similar to rhodeoretine, but soluble in water, $C_{42} H_{36} O_{21}$. When rhodeoretine is acted on by hydrochloric acid, it is resolved into grape sugar, $C_{12} H_{12} O_{12}$, and an oily liquid *rhodeoretinole*, $C_{30} H_{23} O_8$. This reaction places rhodeoretine near to salicine and phloridzine. On the other hand, if we compare 7 eq. of starch, $7 (C_{12} H_{10} O_{10}) = C_{84} H_{70} O_{70}$ with 2 eq. rhodeoretine, $2 (C_{42} H_{35} O_{20}) = C_{84} H_{70} O_{40}$, we can see how this resin may be formed from starch, &c. by deoxidation. *Rhubarb* contains 3 resins, *aporetine*, *phæoretine*, and *erythroretine*. The two first are both $C_{16} H_8 O_7$; the third is $C_{19} H_9 O_7$. They are accompanied by an intensely yellow crystallisable acid, chrysophanic acid, $C_{10} H_8 O_3$, or $C_{40} H_{32} O_{12}$. This latter substance is also found in lichens, such as *Parmelia parietina*, *Squamaria elegans*, &c. *Copal*, which of all the resins is the most insoluble, is said to contain five. Copal varnish is made by adding hot oil of turpentine to copal fused at a gentle heat.

Turf or peat contains several resinous bodies, examined by Mulder. In the turf of Friesland he found 4 resins: *alpha*, $C_{30} H_{40} O_9$; *beta*, $C_{77} H_{67} O_9$; *gamma*, $C_{104} H_{94} O_9$; and *delta*, $C_{131} H_{121} O_9$. A lighter kind of turf from another locality yielded two resins; *alpha* $C_{35} H_{28} O_5$; and *gamma*, $C_{90} H_{84} O_6$.

Resinous varnishes are made by dissolving resins in oil of turpentine and other essential oils; or in drying oils. Spirit varnishes are made by dissolving resins in very strong alcohol.

ACTION OF HEAT ON RESINS.

When resins are distilled in close vessels, they yield a great deal of gas of a high illuminating power, and many volatile liquid compounds of carbon and hydrogen.

Pinic acid yields, when heated, *colopholic acid*. Colophony yields *resineine*, an oil, $C_{20} H_{15} O$; also *retinaphtha*, $C_{14} H_8$, which with chlorine forms a compound $C_{14} H_6 Cl_2$; *retinylène*, $C_{18} H_{12}$, which with sulphuric acid yields an acid, isomeric with sulphocumenic acid, $C_{18} H_{11} S_2 O_5, HO$; *retinole*, $C_{32} H_{16}$; and finally a solid product, *retisterène*, fusible at 152°, having the same composition as naphthaline, $C_{20} H_8$.

COLOURING MATTERS CONTAINING NO NITROGEN.

1. Yellow colouring matters.

The following are the most important of the yellow vegetable colouring matters, many of which are used in dyeing.

Curcumine, from the root of *Curcuma longa*, is resinous, and is dissolved by alkalies, which change it to brown. Hence it is used as a test for alkalies, under the name of *turmeric*. *Gamboge yellow* is extracted from gamboge, the dried juice of *Garcinia gambogia*. It is resinous and powerfully purgative. *Annotto* or *Anatto* is obtained from the seeds of *Bixa orellana* and *Metella tinctoria*. *Carotine* is the colouring matter of the carrot, *Daucus carota*. *Rhabarberine* is a name formerly given to the yellow acid of rhubarb, now called *chrysophanic acid*, which is found also in lichens as above stated. It has great colouring power, and yields a fine violet with alkalies. It is fusible and volatile. Formula, $C_{10} H_8 O_3$. From occurring in *Parmelia parietina*, it has also been called *parietine* and *parietinic acid*. *Luteoline*, the colouring principle of *Reseda luteola* or *Woad*, is volatile and crystallisable. *Quercitrine*, from the bark of *Quercus tinctoria* is crystalline, and its composition is $C_{16} H_8 O_9$, HO. Other yellow colouring matters are *Morine*, from *Morus tinctoria; Safflower yellow*, from *Carthamus tinctorius; Polychroite* from *Saffron*, and others of less interest.

2. Red colouring matters.

Draconine, or Dragon's blood, is a red gum resin, from *Dracæna draco.* It is much used to colour varnishes. *Santaline*, the colouring matter of *Pterocarpus santalinus*, is also resinous, and has an intense red colour. *Anchusine*, from *Anchusa tinctoria*, is the source of the colour of alkanet; it is resinous and yields violet vapours when heated. *Carthamine* is the red colouring matter of safflower, *Carthamus tinctorius.* It is a very fine and intense red, much used for dyeing rose colour, for pink saucers and for rouge, at least the *rouge végétale.*

Madder, the root of *Rubia tinctorium*, contains three different red colouring matters, *madder purple, red*, and *orange.* All three are volatile, and the sublimed crystals of madder red, which are of a fine orange red colour, are called *alizarine.* This is the substance which yields the turkey red dye. With alkalies it yields purple or violet colour, with acids yellow. When dissolved in hot water or alcohol, alizarine yields rose-coloured solutions. The composition of pure madder red is unknown.

Hæmatoxyline is the red of *logwood, Hæmatoxylum campechianum.* It is soluble in water and alcohol, and yields orange crystals, which give to water a red colour, brightened by acids and turned to a violet or blue by alkalies. With alum, logwood yields various shades of violet; with an iron mordant, grey and black. Black cloth and hats are dyed with it, which is the reason they are reddened by acids. According to Erdmann, pure hæmatoxyline is pale yellow, and is coloured red by the atmosphere. Its formula he found to be $C_{40} H_{17} O_{15}$. When acted on by ammonia it yields *hæmateine*, which is dark red, and forms with excess of ammonia a splendid purple matter. Hæmateine is $C_{40} H_{15} O_{16}$; and the purple compound with ammonia is $C_{10} H_{15} O_{16} + 2 NH_3 +$aq. *Brazilwood* and *Camwood* yield colouring matters very similar to hæmatoxyline, if not identical with it.

Many flowers contain a red colouring matter, which is turned green by alkalies, and is very fugitive. It is soluble in water and alcohol.

3. Blue colouring matters.

These are chiefly found in flowers and fruits. They are very closely allied to the red of flowers and fruits, which are no doubt often derived from them by the action of acids. They are all turned green by alkalies and red by acids. Such blue colouring matters as are more permanent contain nitrogen, and will be considered hereafter.

4. Green colouring matter. Chlorophyll.

This is the green of leaves. It is of a nature allied to that of wax, soluble in ether and alcohol, insoluble in water. It is very neutral or indifferent in its relations to other substances.

Polychrome is the name given to a peculiar crystalline principle found in some vegetables, such as quassia. It gives to water the quality of exhibiting a curious play of colours, among which blue predominates, like that of the opal, when the solution is viewed by reflected light; 1 part will give this property to 1,500,000 of water. Its formula is said to be $C_{16} H_8 O_9$, HO, which is the same as that of *quercitrine*, and contains 2 eq. of oxygen more than the *aporetine* of rhubarb.

NON-AZOTISED VEGETABLE COMPOUNDS, THE NATURE OF WHICH IS NOT YET ASCERTAINED.

In this subdivision may be included a number of compounds, most of which crystallise and have a bitter taste, but are neutral and cannot yet be referred to any particular series of compounds. Salicine, phloridzine, and rhodeoretine, which would formerly have been here described, are now treated of along with substances allied to them. The substances now to be briefly mentioned have usually been termed the bitter and extractive principles of plants.

Gentianine, from *Gentiana lutea*, forms yellow needles, very bitter. *Menyanthine*, from *Menyanthes trifoliata*, is bitter, but does not crystallise. *Absinthine*, from *Artemisia absinthium* or wormwood, is a semi-crystalline mass, very bitter, soluble in alcohol. *Tanacetine*, from *Tanacetum vulgare*, is very similar to it. *Santonine* is a beautifully crystallisable compound, obtained fram *Artemisia contra*. It is soluble in alcohol, bitter to the taste, volatile, and coloured yellow by the action of light. *Populine*, from the bark and leaves of *Populus tremula*, forms white crystals, of a sweetish and acrid taste, coloured red by sulphuric acid. It may possibly be connected with salicine. *Liriodendrine* is a crystalline bitter substance, from the bark of *Liriodendron tulipifera*. *Picrolichenine* is an intensely bitter crystalline compound, found in the lichen *Variolaria amara*. It is principally febrifuge. In contact with ammonia and without the access of air, it is changed into a reddish-yellow matter, which finally deposits yellow crystals, not bitter. With access of air, it yields with ammonia a deep-red very soluble matter. *Cetrarine* is another bitter principle, from the lichen, *Cetraria Islandica*, or Iceland moss. It is coloured deep-blue by hydrochloric acid. It is said also to be febrifuge. *Ilicine*, from *Ilex aquifolium*, forms brownish-yellow crystals very bitter and febrifuge. *Syringine* is the bitter principle of the lilac, *Syringa vulgaris*. It is crystalline and soluble in alcohol. *Daphnine* is a bitter crystalline substance, obtained from *Daphne Mezereon*. *Hesperidine* is a crystalline body found in the spongy envelope of oranges and lemons. *Elaterine* is the active principle of *Momordica elaterium*, is crystalline, bitter, and very purgative. Its formula is $C_{20}\ H_{14}\ O_5$. *Colocynthine*, the active principle of colocynth, is amorphous, intensely bitter and purgative. *Bryonine*, from *Bryonia alba* and *dioica*, is similar in its properties. *Mudarine* is the emetic principle of *Calotropis mudarii*. It is a brown amorphous matter, the solution of which in water gelatinises at 95° and becomes again liquid on cooling. *Scillitine* is the bitter of *Scilla maritima*. It is amorphous, bitter, purgative and emetic. *Cathartine* is the bitter purgative principle of senna. *Antiarine*, $C_{14}\ H_{15}\ O_5$, is the active principle of the poison called *Upas antiar*. It is, when introduced into a wound, especially along with soluble matters such as sugar, a most powerful poison, and hitherto no means are known by which its fatal action can be arrested.

Zanthopicrine is a bitter crystalline substance from the bark of *Zanthoxylum Clava Herculis*. It has been little studied. *Picrotoxine*, the bitter principle of *Menispermum cocculus* (*Cocculus indicus*), forms white prisms. The composition of these is not certain, and recent researches seem to show that picrotoxine is a vegetable base, and contains nitrogen, like all that class of compounds. *Columbine* is a crystalline bitter substance, obtained from *columbo*, the root of *Menispermum palmatum*, and somewhat analogous to picrotoxine. *Quassine* is a yellow, crystalline, and very bitter substance from the wood of *Quassia amara*. Its formula is said to be $C_{20}\,H_{12}\ O_6$. *Lupuline*, the bitter principle of hops, is not crystallisable. *Lactucine* is a crystalline resinoid bitter substance, from the juice of *Lactuca virosa* (*Lactucarium*). It has anodyne properties. *Ergotine* is an uncrystallised brown powder, extracted from ergot of rye by hot alcohol, after the fatty matters have been removed by ether. It appears to be poisonous, and is probably the active matter of the ergot. *Porphyroxine* is a crystallisable substance found in Bengal opium. Its solution in diluted acids becomes red when boiled. It requires further investigation. *Saponine* is a peculiar principle, found in the root of *Saponaria officinalis.* It is white, amorphous, and has a taste first sweet, then styptic, and finally acrid. It is a powerful sternutatory. It is soluble in water, and its solution, even when much diluted, froths when agitated, like a solution of soap. The root is used as a detergent. When acted on by alkalies, it is converted into an acid, saponic acid, $C_{26}H_{23}O_{12}$. *Asparagine,* $C_8H_8N_2O_6, 2HO$, is a crystallisable substance found in asparagus, in *Althæa officinalis,* and in other plants, especially those grown in the dark. When boiled with alkalies it loses ammonia, NH_3, and forms *aspartic acid,* $C_8H_5NO_6, 2HO$, which is a bibasic acid. The crystals of asparagine are very large, colourless, and transparent, also hard and brittle. Not only alkalies, but acids and ferments transform it into aspartic acid and ammonia. *Smilacine* is a crystalline substance, found in *Smilax sarsaparilla.* Its composition is $C_{15}H_{13}O_5$. In *China nova* there is found a substance very analogous to smilacine, the composition of which is $C_{15}H_{12}O_4$: that is, smilacine, *minus* 1 eq. water. *Senegine* is an acrid and astringent substance, found in *Polygala senega.* It excites sneezing powerfully. Formula, $C_{22}H_{18}O_{11}$. *Guaiacine* appears to be the active principle of guaiacum. It is acrid and bitter. *Plumbagine,* extracted from the root of *Plumbago europæa,* forms yellow prisms, the taste of which is first sweet and stypic, then acrid and hot. The yellow colour of its aqueous solution is turned cherry-red by alkalies. *Cyclamine* is a crystalline matter from the root of *Cyclamen europæum.* It is very acrid, purgative, and emetic. *Peucedanine* is a very acrid crystalline principle derived from the root of *Peucedanum officinale.* Formula, C_4H_3O. *Imperatorine,* $C_{24}H_{12}O_5$, is a crystallisable compound, obtained from the root of *Imperatoria ostruthium.* It is very acrid and styptic. *Phillyrine,* from the bark of various species of *Phillyrea,* crystallises in silvery scales, which are bitter. *Fraxinine,* from the bark of *Fraxinus excelsior,* is a crystallisable bitter principle. *Tanghine* is a similar substance from *Tanghinia madagascariensis.* It is poisonous. *Melampyrine* is a tasteless, neutral, crystalline substance, from *Melampyrum nemorosum.* *Meconine* is a neutral, crystalline compound contained in opium. It is soluble in water, alcohol, and ether. It is acrid to the taste, fusible, and volatile. Formula, $C_{10}H_5O_4$. With nitric acid it yields *nitromeconine* or *nitromeconic* acid, $C_{20}H_9NO_{12}$. As meconine may be $C_{20}H_{10}O_8$, nitromeconine is $C_{20}\left\{\begin{matrix}H_9\\NO_4\end{matrix}\right.O_8$; in which 1 eq. hydrogen is replaced by 1 eq. nitrous acid. Chlorine transforms meconine into crystals containing chlorine, which, however, by the action of alkalies, yield an acid free from chlorine, mechloic acid, $C_{14}H_7O_{10}$?

Cubebine, $C_{34}H_{17}O_{10}$, is a crystalline compound contained in cubebs. *Olivile*, $C_{12}H_9H_4$, is a crystallisable acrid substance, found in the gum of the olive-tree. *Olivine* is another crystalline matter found on the leaves of the same plant. It is bitter. *Cnicine* is a crystalline matter, found in *Centaurea benedicta*, and in the numerous family of the *Cynarocephalæ*. It is neutral and bitter, and very similar to columbine. Its formula is $C_{28}H_{18}O_{10}$, or $C_{42}H_{27}O_{15}$? and in some respects it approaches to salicine and phloridzine; but it requires further investigation. *Limonine*, or *Limone*, a bitter crystalline matter found in the seeds of oranges, lemons, &c., is $C_{42}H_{25}O_{13}$, when reduced to 42 eq. carbon. This would be Cnicine, *minus* 2 eq. water. *Angelicine* is a crystallised compound found in angelica root.

Besides the above, which have merely been briefly catalogued for want of space, at least an equal number of substances, chiefly crystallisable, and either bitter, acrid, or in a few cases tasteless, have been extracted by various chemists from many different genera and species of plants, but have been so little examined hitherto that we cannot safely describe them as distinct and peculiar.

NITROGENISED COLOURING MATTERS, AND ALLIED SUBSTANCES.

There are several fine and valuable colours, which contain nitrogen as an essential element, and probably in the form of ammonia or amide. Such colours are *archil*, *litmus*, and *cudbear*, derived from certain species of lichens; and *indigo*, derived from the juice of various plants, especially different species of *indigofera*. All these colours are derived from colourless compounds, frequently of an acid nature, by the combined action of air and ammonia. Of these colourless substances, the most important are, *lecanoric acid*, *erythric acid*, and *orcine*.

1. *Lecanoric acid*, or *Lecanorine*, occurs in *Lecanora tartarea*, *Variolaria lactea*, and other lichens. It is extracted by ether, along with another acid, *parellic acid*, and a fatty matter coloured green by chlorophyll. It forms minute white crystals, insoluble in water, soluble in alcohol and ether. Its formula is $C_{18}H_8O_8, HO = C_{18}H_9O_9$. When heated to 212° it becomes anhydrous, $C_{18}H_8O_8$. When heated with alkalies, such as baryta, a carbonate is deposited, and a sweet substance remains dissolved, which crystallises on evaporation. This is *orcine*, which is formed along with carbonic acid, according to the following equation:—

$$\underbrace{C_{18}H_8O_8}_{\text{Anhydrous lecanoric acid.}} = 2CO_2 + \underbrace{C_{16}H_8O_4}_{\text{Anhydrous orcine.}}$$

The same change takes place when lecanoric acid is boiled with water, and for this reason orcine alone is obtained when the lichens are extracted by that solvent.

By the combined action of air and ammonia, lecanoric acid is gradually changed into a deep rich blue or purple mass. Here orcine is first produced, and by the action of ammonia on that compound, orceine, the blue compound, is formed. When heated, lecanoric acid yields a sublimate of anhydrous orcine. When boiled with alcohol, it is gradually converted into the following compound.

2. *Lecanorate of oxide of ethyle.* Syn. *Pseudoerythrine of Heeren; Erythrine of Kane.*—This compound is formed when lecanoric acid and the lichens containing it are boiled with alcohol. It is soluble in hot water, from which it crystallises on cooling, and the solution, after long boiling, contains orcine. It may be sublimed unchanged, and when boiled with alkalies it yields alcohol, carbonic acid, and orcine. Its true nature was discovered by Schunck, who also first detected lecanoric acid. Its formula is $C_{22}H_{13}O_9 = C_4H_5O + C_{18}H_8O_8$.

Lecanorate of oxide of methyle is analogous to the preceding compound.

3. *Orcine* forms large transparent crystals, is very soluble in water, and has a sweet taste. When anhydrous, it may be distilled unchanged. When mixed with ammonia, and exposed to the air, it gradually acquires a deep blood-red colour, forming a nitrogenised colouring matter, *orcéine,* soluble in ammonia with a deep red, in fixed alkalies with a rich violet colour, the formula of which is $C_{16}NH_9O_7$. The production of anhydrous orcine from lecanoric acid, by boiling with baryta, or even by boiling with water, has been described above. But the crystals of orcine, as deposited from its aqueous solution, are a hydrate, $C_{16}H_{11}O_7 = C_{16}H_8O_4 + 3HO$. It is this hydrate which, with the addition of 5 eqs. of oxygen, and 1 eq. of ammonia, yields orceine and water.

$$\underbrace{C_{16}H_{11}O_7}_{\text{Hydrated orcine.}} + O_5 + NH_3 = \underbrace{C_{16}NH_9O_7}_{\text{Orceine.}} + 5HO$$

Orcine forms with oxide of lead a compound, the formula of which is $C_{16}H_8O_4 + 3\,Pbo$.

4. *Parellic acid.*—This acid accompanies lecanoric acid. It forms either minute crystals, the formula of which is $C_{21}H_8O_{10}$, or large hydrated crystals, which are transparent and

of great density. The formula of the latter is $C_{21}H_9O_{11} = C_{21}H_8O_{10}, HO$. When heated to 212°, both kinds lose water and become $C_{21}H_7O_9$, which is probably the formula of the anhydrous acid.

With ammonia, parellic acid becomes brown, and when heated with fixed alkalies, it yields carbonic acid, and other products, not investigated.

5. *Erythric acid.* SYN. *Erythrine of Heeren; Erythriline of Kane; Orcino-lecanoric acid.* This acid is found in *Parmelia roccella*, and *Roccella tinctoria*, the latter being the lichen which yields the best *archil.* It may be extracted by hot water, and purified by alcohol. It crystallises from alcohol in stellated groups. Its solutions are decomposed by boiling, yielding a bitter compound, picroerythrine. When heated, it yields a sublimate of orcine, and when boiled with alkalies, it is resolved into carbonic acid and orcine. When boiled with alcohol, it yields lecanorate of oxide of ethyle. All these facts indicate a close relation to lecanoric acid, and Schunck, who discovered the erythric acid, has pointed out that its formula, $C_{34}H_{19}O_{15}$, represents a compound of 1 eq. lecanoric acid, and 1 eq. orcine. It is probably therefore a coupled acid, orcino-lecanoric acid.

$$\underbrace{C_{18}H_8O_8}_{\text{Lecanoric acid.}} + \underbrace{C_{16}H_{11}O_7}_{\text{Hydrated orcine.}} = \underbrace{C_{34}H_{19}O_{15}}_{\text{Orcino-lecanoric acid.}}$$

It combines with 4 eqs. of oxide of lead, three of which probably unite with the orcine, and the fourth with the lecanoric acid. When boiled with alcohol, it is resolved into lecanoric acid, which unites with oxide of ethyle, and orcine, which is found in solution. It must also yield orcine in large quantity when boiled with baryta, in which case it loses 2 eqs. of carbonic acid, and takes up 3 eqs. of water.

$$\underbrace{C_{34}H_{19}O_{15}}_{\text{Erythric acid.}} + 3\,HO = \underbrace{2\,(C_{16}H_{11}O_7)}_{\text{Hydrated orcine.}} + 2\,CO_2$$

In other words, the orcine ready formed is separated, and the lecanoric acid undergoes the change formerly described.

Erythric or orcino-lecanoric acid is the most important of all the principles found in lichens; but from the facility with which it is altered by boiling with water or alcohol, but little of it can be extracted unchanged. When acted on by ammonia, so as to yield the blue matter of orchil, the lichens containing this acid obviously yield a large proportion of the compound of orceine with ammonia, on which the colour depends. Hence their superior quality.

Variolarine is the name given to a substance obtained by Robiquet from *Variolaria dealbata*. It has been little studied, and is probably identical with some of the compounds above described.

6. *Picroerythrine*. Syn. *Erythrin-bitter of Heeren. Amarythrine of Kane.*—This compound is formed when erythric acid, or the lichens containing it, are boiled with water, and is the cause of the bitter taste of the decoction. When boiled with baryta it yields orcine and carbonate of baryta, and when heated, it yields a sublimate of orcine. This is easily explained by its formula, which is $C_{34} H_{24} O_{20}$, that is, erythric acid, *plus* 5 eqs. of water. For the exact knowledge of all the preceding substances we are indebted to the recent researches of Schunck.

7. *Usnic Acid.*—This acid is found in many lichens, such as *Lichen rangiferinus*, and in many species of *Usnea, Ramalina, Parmelia, Biatora, Lecidea, Alectora, Evernia,* and *Cladonia*. It is extracted by ether, and forms sulphur yellow crystals, insoluble in water and alcohol. Like the other acids of the lichens, it yields coloured compounds under the influence of air and ammonia or fixed alkalies; but these appear to contain no nitrogen, and are not blue or purple, but red. It cannot be made to yield orcine, so far as is yet known. Its formula is $C_{38} H_{17} O_{14}$, which corresponds to 2 eqs. of lecanoric acid, *plus* $C_2 H_2$, and minus O_2.

8. *Chrysophanic Acid.*—This is another crystallisable acid found in *Parmelia parietina*. It forms golden yellow crystals, and with alcoholic solutions of potash and ammonia yields a splendid red colour. Its formula is $C_{10} H_8 O_3$, that is $\frac{1}{2}$ ($C_{20} H_{16}$) naphthaline, *plus* 3 eqs. of oxygen. Its salts are blue or violet when dry, red in solution. This acid has also been found in rhubarb by Schlossberger and Doepping. This and the preceding acid were discovered in the lichens by Rochleder and Heldt.

9. Archil contains, according to Kane, two blue compounds, which he calls *alpha-orcéine* and *beta-orcéine*, $C_{18} H_{10} NO_5$, and $C_{18} H_{10} NO_8$; besides a third of an acid nature, *erythroleic acid*, $C_{26} H_{22} O_8$.

10. Litmus contains, according to Kane, a red fluid, *erythroleine*, $C_{26} H_{22} O_4$; and three solids, of a purple colour, *erythrolitmine*, $C_{26} H_{23} O_{18}$; *azolitmine*, which contains nitrogen, and is the principal constituent of litmus; and *spaniolitmine*, $C_{18} H_7 O_{16}$. According to Gélis, litmus contains three colouring matters, one soluble in ether, which is orange red; one soluble in alcohol, blood red, and one soluble

in water. The second is the chief ingredient of the dye. All give blue compounds with alkalies.

11. *Phloridzéine* is the deep blue compound formed from phloridzine by the action of air an ammonia. Its formula is $C_{42}H_{29}N_2O_{26}$.

12. Indigo.

This valuable dye has been long known; but it is only since 1827 that its chemical relations have been accurately studied. No substance in the whole range of chemistry has yielded a greater variety of most interesting products; and the study of the metamorphoses of indigo has already thrown much light on the laws of the decomposition of organic substances. For what is known on this subject, we are indebted, first, in point of time, to Chevreuil, Runge, Walter Crum, Liebig, Berzelius, and Dumas; more lately, and in an especial manner, to the comprehensive researches of Erdmann, Fritzsche, and Laurent; the last of whom has made known several interesting series of new compounds derived from indigo, and has both confirmed and extended, as well as corrected, in some cases, the previous results obtained by Erdmann; still more recently, Hoffmann and Muspratt have greatly extended our knowledge of the derivatives of indigo.

Indigo is obtained from various plants, chiefly of the genus *indigofera*, as *I. tinctoria*, *anil*, *argentea*, &c., but also of other genera, as *Nerium*, *Isatis*, *Pergularia*, *Gymnema*, *Polygonum*, *Tephrosia*, *Amorpha*, and others. In the juice of these plants, it exists in the form of a colourless soluble compound, probably a compound of white indigo with an alkali. When exposed to the air, it is converted into the blue compound, and becomes at the same time insoluble, just as in an artificial solution of white or reduced indigo in an alkali. The manufacture of indigo is not thoroughly understood, but it would appear that ammonia, as well as air, contributes to the formation of the colour, probably by converting into white indigo some compound present in the fresh juice, the nature of which, however, is still uncertain. In the Antilles and in the East Indies, the leaves are made to ferment in water, during which much ammonia is formed, and the indigo is found in the soluble state, ready to become blue and insoluble by absorbing oxygen. But in North America, the dried leaves are infused in warm water, or boiled with water, till the liquid becomes green, when, on exposure to the air, it deposits blue insoluble indigo. Here the same change must, in great part at least, have taken place during the drying, as during the fermentation of the other process.

The indigo of commerce is a deep blue powder, often cohering in cakes, and exhibiting, when polished by rubbing with the nail or any hard substance, a coppery colour and lustre. It is tasteless and inodorous, insoluble in water, and nearly so in alcohol and ether. It may be purified by treating it successively with boiling diluted sulphuric acid and with water, which remove a glutinous matter; with aqua potassa, at a gentle heat, which dissolves a brown colouring matter; and with boiling alcohol, which takes up a red colouring matter. When fresh alcohol becomes no longer red, but blue, the indigo is as pure as it can be made by such means.

To purify it still further, it is digested with water, lime, and grape or starch sugar, which deoxidises or reduces the indigo, while the lime combines with the reduced indigo, forming a soluble compound, of a wine yellow tint. This being filtered into dilute hydrochloric acid, which removes the lime, deposits pure indigo as a blue powder. Cloth steeped in the above solution of indigo, and exposed to the air, is quickly dyed blue, as the indigo, at the moment of being rendered insoluble, combines with the fibre of the cloth, to which it adheres very firmly, so that it cannot be washed away. If indigo, grape sugar, soda, and alcohol, be digested together in proper proportions, a yellow solution is obtained, which, when exposed to air, deposits pure indigo in crystals. (Fritzsche.)

Pure indigo, when rapidly heated on a slip of platinum, volatilises, yielding purple vapours, which condense in purple crystals on a cold surface. These crystals are called Indigotine: but they are nothing else than sublimed indigo, and have all the chemical characters of pure indigo. When distilled, indigo yields, among other products common to all nitrogenised organic matters, a very curious oily liquid, of powerfully basic properties, and forming salts with acids which crystallise with singular facility. This base is *aniline* (*benzidam*, *crystalline*, *kyanol*), and is found in the oil of coal tar, as well as in the products of distillation of many nitrogenised bodies.

Oil of vitriol dissolves indigo with a deep blue colour, forming two blue acids. This solution is much used in dyeing. Nitric acid, chloric acid, chromic acid, chlorine and bromine, all dissolve indigo, giving rise to oxygenised and chlorinised or brominised products, all of which are yellow and orange-coloured. When boiled with strong aqua potassa, indigo is also oxidised and dissolved in the form of new acids.

When placed in contact with deoxidising or reducing agents, such as protosalts of iron, tin, and manganese, or honey and grape sugar, along with an alkali such as soda or lime, indigo is decolorised and dissolved in combination with the alkali. The addition of diluted hydrochloric acid, air being carefully excluded, precipitates *reduced* or *white indigo.*

White or *reduced indigo*, $C_{16} H_6 N O_2$, obtained as above described, is a crystalline powder of a dirty white, which, if washed with water previously boiled to expel air, and cooled in closed vessels, and dried in vacuo, is bluish externally, but grey within. The blue parts being removed, the remainder is reduced indigo. When moist, it very rapidly passes into blue indigo, oxygen being absorbed: when dry, the change is more slowly effected. It is insoluble in water and acids, very soluble in alkaline solutions; its solutions, if exposed to the air, deposit pure indigo blue, as a powder.

The first accurate analysis of indigo blue was made by Walter Crum; and his results have been confirmed by all succeeding experimenters. The formula now adopted for indigo, as agreeing best with its numerous metamorphoses, is one first proposed by Dumas; namely, $C_{16} H_5 N O_2$. This formula is the same with that of cyanide of benzoyle, or of benzile, $C_{14} H_5 O_2 + C_2 N = C_{16} H_5 N O_2$.

The relation of white indigo to blue indigo is, according to one view, the same as that of hyduret of benzoyle to benzoyle, or of alloxantine to alloxan. Thus we have

Benzoyle	$C_{14} H_5 O_2$	Hyduret of Benzoyle	$C_{14} H_5 O_2 + H$
Alloxan	$C_8 H_4 N_2 O_{10}$	Alloxantine . .	$C_8 H_4 N_2 O_{10} + H$
Indigo blue	$C_{16} H_5 N O_2$	Indigo white . .	$C_{16} H_5 N O_2 + H$

According to another hypothesis, white indigo is the hydrate of an inferior degree of oxidation of the same radical of which blue indigo is the higher oxide. Blue indigo, on this view, is $C_{16} H_5 N + O_2$, and white indigo is a hydrate $C_{16} H_5 N + O + HO$. This latter view is the more probable, not only in regard to indigo, but also in regard to alloxan, for, assuming *uryle* to be $C_8 N_2 O_4 = Ul$, alloxan will be $Ul + O_2 + 4 HO$, and alloxantine will be $Ul + O + 5 HO$.

The action of grape sugar, in reducing indigo, tells in favour of the latter hypothesis. For if white indigo is blue indigo *plus* hydrogen, this hydrogen is derived from water, the oxygen of which must have combined with the hydrogen of the sugar (to convert the sugar into formic acid, which is produced in this operation). Here, then, we should have oxygen leaving hydrogen to combine with hydrogen, or, in other words, water produced and decomposed at the same time, which is in the highest degree improbable. To demonstrate this, let the radical of indigo be assumed to be Anyle $= C_{16} H_5 N = An$: let blue indigo be AnO_2, and white indigo AnO_2, H or AnO, HO. Then 12 eq. of blue indigo, 12 of water, and 1 of grape sugar, act on each other, and, according to the view which makes white indigo the hyduret of blue indigo, the reaction is as follows: $12\,AnO_2 + 12\,HO + C_{12}H_{12}O_{12} = 12\,(AnO_2, H) + 6\,(C_2HO_3) + 6\,HO$. In this explanation it is evident that 6 eq. of oxygen have quitted hydrogen to combine with hydrogen. On the other view, the reaction is as follows, free from any such absurdity: $12\,AnO_2 + 12\,HO + C_{12}H_{12}O_{12} = 12\,AnO, HO + 6\,(C_2HO_3) + 6\,HO$. Here the 12 eq. of deutoxide of anyle (blue indigo) lose 12 eq. oxygen, which are replaced by 12 eq. water; and the 12 eq. oxygen acting on the sugar, 6 eq. take 6 eq. hydrogen, forming water, and 6 eq. convert the residue into formic acid. The student will bear in mind that C_2HO_3 is the formula of formic acid, and $C_{12}H_{12}O_{12}$ that of dry grape sugar.

We shall therefore consider white indigo as the hydrated protoxide of anyle ($C_{16}H_5N, O + HO$), and blue indigo as the anhydrous deutoxide ($C_{16}H_5N, O_2$). White indigo forms compounds with bases, in which, no doubt, its hydratic water is replaced by an equivalent of metallic oxide, as in the general formula, $C_{16}H_5N, O + MO$.

ACTION OF SULPHURIC ACID ON INDIGO.

When powdered pure indigo is added to 15 parts of oil of vitriol, and gently warmed, a deep blue solution is formed, which mixes perfectly with water. But if only 8 or 10 parts of acid are used, the addition of water causes the deposition of a purple powder, while a blue solution is obtained. The purple powder, which, although insoluble in dilute acid, is soluble in pure water, is sulphopurpuric acid; the blue solution contains two acids, sulphoindigotic and hyposulphoindigotic acids. When neutralised with potash, these acids form salts, which separate from the liquid when it is saturated with any alkaline salt, such as acetate or carbonate of potash. The two blue salts may be separated from each other by alcohol, but the composition of the hyposulphoindigotate of potash is not known. The sulphoindigotate appears to be strictly a hyposulphoindigotate, and its formula is in all probability $C_{16}H_4NO_2, S_2O_5 + KO$. Here the indigo has lost 1 eq. of hydrogen, and the 2 eq. sulphuric acid 1 eq. oxygen. Dumas's view, according to which the salt is a double sulphate, analogous to sulphovinate of potash, $C_{16}H_4NO, SO_3 + KO, SO_3$, is not supported by the chemical relations of these substances. Dumas conjectured that indigo blue was analogous to alcohol, and that its formula was $C_{16}H_4N,O + HO$, the body $C_{16}H_4N,O$ being analogous to oxide of ethyle. But, as already stated, this view is far-fetched, and does not agree with the chemical relations of indigo. It would make, for example, white indigo $C_{16}H_4N,O + H + HO$ or $C_{16}NH_4 + 2HO$, both most improbable formulæ.

The blue solution of indigo in oil of vitriol, if diluted and digested with flannel or woollen cloth, is entirely deprived of blue colour, while the cloth is so effectually dyed that the colour cannot be washed out. It can, however, be dissolved from the cloth by carbonate of ammonia, and by this means the sulphoindigotates of ammonia, and from these the other salts of the blue acids, are prepared.

The sulphopurpuric acid, according to Dumas, contains the elements of 2 eq. sulphuric acid and 2 eq. indigo, and neutralises only 1 eq. of base. But the indigo in it has probably lost hydrogen (while the acid has lost oxygen), or hydrogen and oxygen.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine, $C_{16}H_5NO_4$. This interesting compound, which is blue indigo, *plus* 2 eq. oxygen, is formed by digesting indigo along with water, sulphuric acid, and bichromate of potash, or by heating indigo with weak nitric acid. It dissolves, and the solution on evaporation deposits aurora-red crystals of isatine, sparingly soluble in cold water, more soluble in hot water and in alcohol. By the action of chlorine, it yields two compounds in which hydrogen is partially replaced by chlorine. It may be volatilised if heated on a plate of metal. When acted on by a strong solution of potash, isatine is dissolved with an intense violet colour, which on addition of water and evaporation changes to yellow, and the liquid deposits pale yellow crystals, which contain potash, united to a new acid, isatinic acid, formed from isatine by the addition of 1 eq. water. When separated from its salts by stronger acids, isatinic acid is at once resolved into isatine and water; but if isatinate of lead be decomposed by sulphuretted hydrogen, and the filtered solution evaporated spontaneously in vacuo, the acid is obtained as a white flocculent powder, which, when dissolved in boiling water, instantly becomes red, and the solution on cooling deposits crystals of isatine. Isatinic acid is $C_{16}H_6NO_5\,HO$. Its salts have the formula $C_{16}H_6NO_5, MO$. The violet-coloured compound first formed when isatine acts on potash is a compound of isatine and potash, which, when heated with water, soon passes into isatinate of potash.

With sulphurous acid, or rather sulphites, isatine forms salts of the formula $C_{16}H_5NO_4, 2SO_2 + MO$; which may be formed also by the action of sulphurous acid on isatinates.

By the action of chlorine, isatine is converted into two compounds, chlorisatine and bichlorisatine. When chlorine is passed through isatine or indigo suspended in water, both these compounds are formed, and they are separated by crystallisation, chlorisatine being the least soluble of the two.

Chlorisatine, $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4$, forms transparent orange yellow 4-sided prisms, isomorphous with isatine, and very analogous to it in all respects. When acted on by potash, there is first formed a deep red solution, which when heated soon becomes yellow, and on cooling deposits brilliant pale yellow crystals of *chlorisatinate of potash*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5, KO$, a salt perfectly analogous to isatinate of potash, and containing an acid, chlorisatinic acid, which is chlorisatine, *plus* 1 eq. water, $C_{16}H_5ClNO_5$. Like isatinic acid, when separated from its salts it is speedily resolved into chlorisatine and water. *Chlorisatinate of silver*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5, AgO$ forms yellow crystals, soluble in hot water. *Chlorisatinate of baryta*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5, BaO, + 3aq.$ forms golden yellow tables. *Chlorisatinate of lead*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5, PbO$, when first precipitated from the salt of potash by nitrate of lead, forms a gelatinous yellow precipitate, which soon becomes flocculent, acquiring a splendid scarlet colour. The red salt is crystalline, the yellow amorphous. Chlorisatinate of copper forms at first a brownish yellow bulky precipitate, which soon changes to a heavy granular blood-red powder.

Like the isatinates, the chlorisatinates combine with the sulphurous acid, forming salts of the formula $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4, 2SO_2 + MO$. In short, the analogy between isatine and chlorisatine, isatinates and chlorisatinates, &c. is such as to furnish a very beautiful example of the substitution of chlorine for hydrogen, while the type or chemical character of the compound is unaffected. In bichlorisatine, we shall see an additional example of the same truth.

Bichlorisatine, $C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.NO_4$, is formed along with the preceding compound. It is more soluble than chlorisatine, but is otherwise remarkably similar to it. With aqua potassæ it first forms a deep red solution (here, as in the case of isatine and chlorisatine, a compound of it with potash), which, when heated, changes to yellow, and on evaporation yields yellow scales of a salt composed of potash and *bichlorisatinic acid.* The acid may be separated by stronger acids as a yellow powder, which when dissolved and warmed is resolved into bichlorisatine and water. Its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5, HO$. The salt of *baryta,* $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5, BaO$, forms golden yellow needles. The salt of *copper* is at first bulky and brown, but soon becomes greenish-yellow and crystalline, and finally, a heavy granular powder of a fine carmine red colour.

Bichlorisatine with sulphites forms compounds analogous to those above mentioned of isatine and chlorisatine. In this case also, therefore, the type is perfectly retained, although 2 eq. of the hydrogen of isatine have been replaced by chlorine.

Bromine acts on isatine, and forms two compounds, *bromisatine* and *bibromisatine,* entirely analogous to chlorisatine and bichlorisatine, forming *bromisatinic* and *bibromisatinic* acids, and also compounds with sulphites analogous to those just mentioned. We have, therefore, from isatine and isatinic acid, by substitution, the following compounds:

Isatine	$C_{16}\ H_5\ NO_4$
Isatinic Acid	$C_{16}\ H_6\ NO_5 + HO$
Chlorisatine	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4$
Chlorisatinic Acid	$C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_5 + HO$
Bichlorisatine	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. NO_4$
Bichlorisatinic Acid	$C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5 + HO$
Bromisatine	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right. NO_4$
Bromisatinic Acid	$C_{16}\left\{\begin{matrix}H_5\\Br\end{matrix}\right. NO_5 + HO$
Bibromisatine	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right. NO_4$
Bibromisatinic Acid	$C_{16}\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right. NO_5 + HO$
Isatinosulphites	$C_{16}\ H_5\ NO_4, 2SO_2 + MO$
Chlorisatinosulphites	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4, 2SO_2 + MO$

Bichlorisatinosulphites .	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. NO_4, 2SO_2+MO$
Bromisatinosulphites .	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right. NO_4, 2SO_2+MO$
Bibromisatinosulphites .	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right. NO_4, 2SO_2+MO$

Hoffmann has lately shown that isatine when heated with potash, yields *aniline* (see *Aniline*), and that chlorisatine, bromisatine, &c., when treated in the same way, yield compounds of the type of aniline, in which hydrogen is replaced by chlorine, bromine, or both. Some of these compounds retain the basic character, and are therefore very interesting, as the first examples of such chlorinised or brominised bases. A table of the compounds derived by substitution from aniline is given under that substance. Here we have only space to mention that chloraniline, dichloraniline, bromaniline, and dibromaniline, are crystalline volatile bases, forming crystallisable salts, and very analogous to aniline: while in trichloraniline, tribromaniline, chlorodibromaniline, the basic character is lost.

Isatyde, $C_{16}H_6NO_4 = C_{16}H_5NO_4, H$, is formed when an alcoholic solution of isatine is acted on by sulphuret of ammonium. It is a grey crystalline powder, and may be considered to represent isatine *plus* 1 eq. hydrogen.

Sulphésatyde, $C_{16}H_6N\left\{\begin{matrix}O_2\\S_2\end{matrix}\right.$ is isatyde, in which 2 eq. oxygen are replaced by sulphur. It is formed by the action of sulphuretted hydrogen on isatine dissolved in alcohol, and is a greyish-yellow amorphous powder. *Sulphisatine* is the name of a compound obtained in the same way by Erdmann, which he considers to be different from sulphésatyde.

Chlorisatyde, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_4$, is a white powder somewhat crystalline, obtained by the action of sulphuret of ammonium on chlorisatine. It is perfectly analogous to isatyde. By the action of sulphuretted hydrogen on chlorisatine, a compound is formed which is $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NS_4$; that is chlorisatyde, in which all the oxygen is replaced by sulphur.

Bichlorisatyde, $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right.NO_4$ and *bibromisatyde*, $C_{16}\left\}\begin{matrix}H_4\\Br_2\end{matrix}\right.NO_4$, are perfectly analogous, in formation and properties, to chlorisatyde.

Sulphasatyde, $C_{16}H_6N\left\{\begin{matrix}O_3\\S\end{matrix}\right.$ is formed by the action of potash on sulphésatyde, from which it differs in having only

1 eq. oxygen replaced by sulphur. It is a white crystalline powder.

Indine, $C_{16}H_6NO_2$ is a crystallised substance, of a beautiful rose colour, formed by the action of potash on sulphésatyde, along with the preceding; or by the action of potash on sulphasatyde or isatyde. In the last case, isatinate of potash is also formed, thus, $3\,(C_{16}H_6NO_4) + 2\,KO = 2\,(KO,\,C_{16}H_6NO_5) + C_{16}H_6NO_2$. It is sulphésatyde, *minus* 2 eq. sulphur, and is also isomeric with white indigo. It is decomposed by nitric acid, and by bromine, which give rise to new products.

When indine, moistened with alcohol, is covered with a lukewarm solution of potash, it forms a black solution which in a few moments becomes a semisolid mass of black needles, which are a compound of potash with indine or rather with indinic acid, an acid formed from indine, like isatinic acid from isatine, by the assimilation of 1 eq. water, and which is very easily again resolved into indine and water.

Hydrindine is a yellow crystalline compound formed by heating indine, sulphasatyde, or isatyde with potash. Its composition is $C_{32}H_{13}N_2O_5$, that is 2 eq. indine *plus* 1 eq. water; and when strongly heated, it is resolved into indine and water. It is not composed of these substances, however, for it forms with potash a white salt, hydrindinate of potash. The acid in this salt appears to be formed, like some of those already described, by the addition of water to hydrindine; its formula is probably $C_{16}H_{15}N_2O_7,\ 2\,HO$.

Nitrindine, $C_{16}H_4N_2O_7$, is a beautiful violet-coloured powder formed by the action of nitric acid on indine and hydrindine. It is indine, in which 2 eq. hydrogen are replaced, one by oxygen, the other by nitrous acid; $C_{16}\left\{\begin{matrix}H_4\\NO_4\\O\end{matrix}\right\}NO_2$.

Chlorindine, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_2 + 2\,HO$, is a powder of a dirty violet colour, formed by the action of heat on chlorisatyde. Analogous compounds are obtained from *bichlorisatyde* and *bibromisatyde*. Bichlorindine is like chlorindine. Bibromindine is very dark red, and dissolves in alcohol with a fine purple colour.

The action of potash on isatyde appears to be the type of its action on chlorisatyde, bromisatyde, bichlorisatyde, and bibromisatyde. When isatyde is acted on by potash, it yields isatine (or isatinate of potash); indine (or indinate of potash); and hydrindine (or hydrindinate of potash). 6 eq. isatyde, $(6\,C_{16}$

$H_6 NO_4$) are equal to 4 eq. isatine ($4 C_{16} H_5 NO_4$) + 2 eq. indine ($2 C_{16} H_6 NO_2$) + 4 eq. water: or they are equal to 4 eq. isatine ($4 C_{16} H_5 NO_4$) + 1 eq. hydrindine ($C_{32} H_{13} N_2 O_5$) + 3 eq. water. Both changes probably occur, and the three compounds, isatine, indine, and hydrindine, alike take up the elements of water to form the acids, which, to avoid confusion, are not here expressed. Now there is good reason to believe that precisely analogous changes occur when potash acts on bichlorisatyde and on bibromisatyde, each yielding three corresponding compounds and the three acids derived from these. The reader, by strictly following the analogy of the formulæ given above for the action of potash on isatyde, will easily be able to construct the equations for the other analogous cases.

When sulphésatyde is acted on by bisulphite of ammonia, there is formed among other products not fully investigated, a salt formed of ammonia united to a new acid, *sulphisatanous acid*, quite different from the acid in the salts formed when isatine is acted on by sulphites. This new acid is $C_{16} H_6 NO_3, 2 SO_2 + HO$, or perhaps rather $C_{16} H_6 N \left\{ \begin{array}{l} O_2 \\ 2 SO_2 \end{array} \right\} + HO$; that is, sulphésatyde, in which the 2 eq. of sulphur have been replaced by 2 eq. sulphurous acid.

The action of bisulphite of ammonia on sulphésatyde sometimes gives rise to the formation of different products: among others, to an insoluble white powder, *isatan*, $C_{16} H_6 NO_3$, which when heated yields isatine and indine; $3 (C_{16} H_6 NO_3) = C_{16} H_5 NO_4 + 2 (C_{16} H_6 NO_2) + HO$. Both indine and nitrindine, when acted on by bisulphite of ammonia, appear to produce compounds analogous to those derived from sulphésatyde.

Chlorindopten is the name given by Erdmann to a volatile crystalline substance, formed along with chlorisatine and bichlorisatine, when chlorine acts on indigo. When the chlorinised mass is distilled with water, this substance passes over in white crystals, which are acid, and evidently a mixture of two substances. When this chlorindopten is heated with potash, a neutral substance passes over, in white crystals similar to the original ones; this is *chlorindatmit*; while the potash retains an acid of a disagreeable odour, *chlorindoptenic acid.*

Chlorindoptenic acid, $C_{12} H_4 Cl_3 O, HO$, is separated from its potash salt by acids, as a white flocculent matter of a very disagreeable odour. Laurent has identified it with his chlorophenisic acid, an acid derived from coal tar by the action of chlorine, and makes its formula $C_{12} \left\{ \begin{array}{l} H_2 \\ Cl_3 \end{array} \right\} O, HO$. Chlorindatmit appears to be *trichloraniline*, $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$ (Hoffmann).

By the further action of chlorine on chlorisatine or bichlorisatine, dissolved in alcohol, new compounds are formed, among which are, *chlorinised chlorindopten*, which, like chlorindopten, is a mixture apparently of chlorindatmit, with an acid, *chlorinised chlorindoptenic acid*, $C_{12}\,Cl_5\,O, HO$; which is the *chlorophenusic acid* of Laurent. This acid is accompanied by *chloranile*, $C_{12}\,Cl_4\,O_4$, a neutral body in volatile golden yellow scales, soluble in hot alcohol, which is also derived from the oil of coal tar, or rather from the hydrate of phenyle or carbolic acid of that oil, from which chlorophenisic and chlorophenusic acids are obtained.

Chloranile dissolves in weak potash with a deep purple colour, and the solution deposits dark purplish-red crystals, composed of potash and a new acid, *chloranilic acid*. This acid forms scarlet or yellow crystals, according as it contains water of crystallisation or not. Its formula is $C_{12}\,Cl_2\,O_6$, $2\,HO$, or $C_6\,Cl\,O_3$, HO.

When chloranile is acted on by aqua ammoniæ, it is dissolved, forming a blood-red solution, which deposits chesnut-brown crystals of *chloranilammon*, $C_6\,H_3\,H\,Cl\,O_3 + 4\,aq. = C_6\,Cl\,O_3 + NH_3 + 4\,aq.$ It dissolves in water with a purple colour, and when a saturated solution is mixed with hydrochloric acid, it deposits very brilliant black needles of great length. These are a new compound, *chloranilam*, $C_{12}\,Cl_2\,H_3\,NO_6 = C_{12}\,Cl_2\,O_6 + NH_3$; that is 2 eq. of chloranilammon, $2\,(C_6\,Cl\,O_3, NH_3) = C_{12}\,Cl_2\,O_6, N_2\,H_6$; minus 1 eq. ammonia NH_3. Both these compounds give precipitates with metallic solutions, which are the same from both, but distinct from those formed by chloranilic acid or its salts. Chloranilammon, according to Laurent, is the ammonia salt of an acid containing amide as an ingredient. Chloranilam is the acid itself.

By the action of ammonia on isatine there are produced several new compounds, varying with the strength of the ammonia, and the menstruum employed. In these compounds, oxygen is replaced by *amide*, NH_2, or *imide*, $\frac{1}{2}\,NH = Im$.

Imesatine is formed when dry ammonia is passed through an alcoholic solution of isatine. It forms fine deep yellow crystals, the formula of which is $C_{16}\,H_6\,N_2\,O_2 = C_{16}\,H_5\,N\left\{\begin{matrix}O_2\\Im_2\end{matrix}\right.$.

Imasatine is formed when aqua ammoniæ acts on a solution of isatine in alcohol. It is a greyish-yellow crystalline substance, the formula of which is $C_{16}\,H_5\,N\left\{\begin{matrix}O_3\\Im\end{matrix}\right.$?

Imasatinic acid is formed along with the preceding, and is dissolved along with ammonia. By the addition of an acid it is precipitated as a beautiful scarlet crystalline powder, soluble in hot alcohol, which deposits it in splendid tabular crystals similar to the sublimed periodide of mercury. It dissolves sparingly in acids with a violet colour, and these solutions deposit violet crystals. Its formula is $C_{16}\,H_5\,N\left\{\begin{matrix}O_3\\ \mathrm{Im}\end{matrix}\right\} + HO$.

Amasatine is formed along with the two preceding bodies. It has a fine yellow colour, and dissolves in acids with a violet colour, apparently passing into imasatinic acid. Its formula is $C_{16}\,H_5\,N\left\{\begin{matrix}O_3\\ \mathrm{Ad}\end{matrix}\right\} + HO$ ($\mathrm{Ad} = NH_2$ = amide).

The analogy between chlorisatine, &c., and isatine, holds in regard to the action of ammonia on them. By the action of dry ammonia on an alcoholic solution of chlorisatine there is formed a yellow crystalline compound, analogous to imesatine. It is called *Imechlorisatinase*, and its formula is $C_{16}\left\{\begin{matrix}H_4\\ Cl\end{matrix}\right\}N\left\{\begin{matrix}O_2\\ 2\,HN.\end{matrix}\right.$

Imachlorisatinase is analogous to imasatine. Its formula is $C_{16}\left\{\begin{matrix}H_4\\ Cl\end{matrix}\right\}N\left\{\begin{matrix}O_3\\ NH.\end{matrix}\right.$ It forms brownish-yellow crystals.

Imabromisatinese, formed by the action of dry ammonia on bibromisatine in alcohol, is $C_{16}\left\{\begin{matrix}H_3\\ Br_2\end{matrix}\right\}N\left\{\begin{matrix}O_3\\ NH.\end{matrix}\right.$ It is a deep orange crystalline powder.

We have now briefly run over the catalogue of the very remarkable compounds derived from indigo by the action of sulphuric acid and bichromate of potash, which produces isatine, and by the action of chlorine either on indigo or on isatine, of bromine on the same, and of potash, ammonia, sulphuretted hydrogen and sulphuret of ammonium on the products of these actions. The nomenclature of these compounds is in a very imperfect state, and requires reformation, but this cannot be effected until the substances themselves have been more thoroughly studied. It is most important to observe, that by or through chloranile and the chlorindoptenic acids, the series to which indigo belongs connects itself with that of carbolic acid or hydrate of phenyle (to be afterwards described), and these again with the series of salicyle. We have now to mention one or two products of the action of nitric acid on indigo which are common to all these series, and like chloranile, seem likely to be very frequently met with as products of the decomposition of organic compounds.

Anilic acid, Syn. *Indigotic acid*, *Nitrosalicylic acid*, $C_{14}\,H_4\,N\,O_9,\,HO$. This acid is formed by the long-continued action of weak nitric acid on indigo. It is also formed in the preparation of isatine, if the action be pushed too far. It is identical with nitrosalicylic acid, obtained by the action of nitric acid on salicylic acid or on salicine. It forms fine yellowish-white prisms, which are light and bulky, and shrink much in drying. It is fusible and volatile. By the action of strong nitric acid it is converted into oxalic and picric acids. It requires 1000 parts of cold water for solution. Its salts crystallise well, and their general formula is $C_{14} H_4 N O_9, M O$. The anilate of oxide of methyle is obtained as a crystalline compound by the moderated action of nitric acid on the salicylate of oxide of methyle (oil of gaultheria). The anilate of oxide of ethyle is exactly similar.

Picric acid, Syn. *Carbazotic acid*, *Nitropicric acid*, *Nitrophenisic acid*, $C_{12} \left\{ \begin{matrix} H_2 \\ 3 N O_4 \end{matrix} \right\} O, H O$. This acid is formed by the action of nitric acid on anilic acid, indigo, salicine, salicylic acid, hydrate of phenyle or carbolic acid, coumarine, silk, aloes (?), and other substances. It is most easily formed from carbolic acid, salicine, or oil of gaultheria, by the action of an excess of fuming nitric acid assisted by heat. It is purified by solution in hot water and recrystallisation. It forms pale yellow or even white scales of a silvery lustre. They dissolve in hot water with a strong yellow colour, and a very bitter taste. The acid is fusible and volatile. Its salts crystallise most readily, and all explode when heated. When these salts are put in contact with lime and green vitriol, blood-red solutions are formed, containing the lime salt of a new acid. The picrate of potash is so sparingly soluble, especially in alcohol, that an alcoholic solution of picric acid may be used as a test for potash.

Picric acid is interesting as occurring among the products of the decomposition by nitric acid of so many different substances. It is easily derived from the series of phenyle, that is, from carbolic acid, $C_{12} H_5 O, H O$. Derived from this, we have Chlorophenesic acid, $C_{12} \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right\} O, H O$, Chlorophenusic acid, $C_{12} Cl_5 O, H O$, and Picric acid, $C_{12} \left\{ \begin{matrix} H_2 \\ 3 N O_4 \end{matrix} \right\} O, H O$. It is, therefore, carbolic acid in which 3 eq. of hydrogen are replaced by 3 eq. of nitrous acid.

When indigo is heated with concentrated potash, there are formed two new acids: *chrysanilic acid*, the composition of which is uncertain, and *anthranilic acid*, $C_{14} H_7 N O_4 = C_{14} H_6 N O_3, H O$. The latter is purified in the form of anthranilate of potash, and the acid separated by an excess of acetic acid. It forms transparent yellow scales, which, however, when quite pure, are colourless. It is derived from blue indigo, $C_{16} H_5$

NO_2, by the loss of 2 eq. carbon and the addition of 2 eq. water.

When anthranilic acid is mixed with powdered glass, and rapidly heated, it is resolved into carbonic acid and an oily liquid, which is *aniline*, a very powerful base, devoid of oxygen, identical with the *crystalline* of Unverdorben, and the *kyanol* of Runge, $C_{12}H_7N$. This metamorphosis is very simple: $C_{14}H_7NO_4 = 2CO_2 + C_{12}H_7N$. Since aniline is obtained in many other cases of decomposition of organic matters by heat, it becomes a substance of great interest.

Aniline is recognised by its property of striking a deep violet blue colour with chloride of lime. It obtained the name *kyanol* from this property. Its other name, *crystalline*, indicates its great tendency to form crystallisable salts with acids.

The recent researches of A. W. Hoffmann have greatly extended our knowledge of this remarkable compound. He has shown that it is best obtained by heating isatine with potash, thus $C_{16}NH_5O_4 + 4(KO, HO) = C_{12}H_7N + 4(KO, CO_2) + H_2$. But he has also proved that its formation is not confined to the products of the decomposition of indigo, it being formed when other substances, isomeric with anthranilic acid, are exposed to heat along with bases, such as lime or baryta. Such substances are *salicylamide* and *protonitrobenzoĕne* or *nitrotoluide*, both of which have the empirical formula $C_{14}H_7NO_4$. The former yields little, but the latter is entirely resolved into aniline and carbonic acid. He has also fully identified aniline with the *cystalline* of Unverdorben, a base occurring with others among the products of distillation of animal matter, and in coal tar. It is worthy of remark that a close connection may be traced between aniline and carbolic acid (hydrate of phenyle). The latter is $C_{12}H_5O, HO$. The carbolate of ammonia, $C_{12}H_5O, NH_4O$, minus 2 eq. water would yield an amide, *phenylamide*, which would be $C_{12}H_5NH_2 = C_{12}H_7N$; and this is aniline. Now in Hoffmann's experiment above mentioned, in which salicylamide was heated with lime, it did not yield much aniline, but, on the other hand, it furnished a large quantity of carbolic acid.

It is further to be noticed that carbolic acid (hydrate of phenyle) and aniline (phenylamide) occur together in coal tar; and that all the substances which yield either one or other of these are also converted into picric acid, $C_{12}\left\{\begin{matrix} H_2 \\ 3NO_4 \end{matrix}\right\}O, HO$, by the action of nitric acid. Thus carbolic acid, indigo, salicine, and salicylic acid, are all transformed into picric acid by excess of nitric acid.

Another point in which all these substances agree is this, that when acted on by a mixture of hydrochloric acid and chlorate of potash, they are all converted into chloranile, $C_{12}Cl_4O_4$. It is more than probable that all those bodies, such as indigo, salicine, carbolic acid, &c., which in this way yield chloranile, either belong to the series of phenyle or are nearly allied to that series, and readily pass into it. The fundamental or primitive compound of that series appears to be some compound of the formula $C_{12}\Delta_8$, where Δ stands for hydrogen, chlorine, bromine, iodine, oxygen, nitrous acid, &c. &c. Assuming this, and supposing Δ to be represented by H, then we have the following series, which will exhibit in a practical form the doctrine of substitutions.

$$C_{12}\ H_8 = \text{Supposed origin or nucleus of the series.}$$

$$C_{12}\left\{\begin{matrix}H_6\\O_2\end{matrix}\right\} = C_{12}\ H_5\ O,\ HO = \text{hydrate of phenyle.}$$

$$C_{12}\left\{\begin{matrix}H_4\\Cl_2\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O,\ HO = \text{chlorophenesic acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\Cl_3\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O,\ HO = \text{chlorophenisic acid.}$$

$$C_{12}\left\{\begin{matrix}H\\Cl_5\\O_2\end{matrix}\right\} = C_{12}Cl_5,\ O,\ HO = \text{chlorophenusic acid.}$$

$$C_{12}\left\{\begin{matrix}Cl_4\\O_4\end{matrix}\right\} = \text{chloranile.}$$

$$C_{12}\left\{\begin{matrix}H_7\\N\end{matrix}\right\} = \text{aniline} = C_{12}\left\{\begin{matrix}H_5\\Ad\end{matrix}\right\} = \text{phenylamide.}$$

$$C_{12}\left\{\begin{matrix}H_4\\2\,NO_4\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_3\\2\,NO_4\end{matrix}\right\}O,\ HO = \text{nitrophenesic acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\3\,NO_4\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\3\,NO_4\end{matrix}\right\}O,\ HO = \text{nitrophenisic (picric) acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\Br_3\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}O,\ HO = \text{bromophenisic acid.}$$

Hoffmann has shown that isatine, when distilled with potash, yields aniline; and that chlorisatine, so analogous in all respects to isatine, undergoes a similar decomposition, yielding a new base, *chloraniline;* also that other compounds may be formed containing more chlorine, but still belonging to the same series; that bromisatine also yields a base, bromaniline; finally, that, by the action of ammonia and sulphuretted hydrogen on *binitrobenzide* or dinitrobenzole, there is formed a base, *nitraniline,* in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid, and that in this base 2 eqs. of hydrogen may further be replaced by bromine, yielding a neutral body. The following are the formulæ of these new compounds, which, it will be observed, are still referable to the original formula, $C_{12}\,\Delta_8$ or $C_{12}\,H_8$.

Aniline	$C_{12}\ H_7\ N$	basic.	Amaphenase.
Chloraniline	$C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N$	basic.	Amachlophenese.
Dichloraniline	$C_{12}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right\}N$	basic.	Amachlophenise.
Trichloraniline	$C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$	neutral.	Amachlophenose.
Bromaniline	$C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N$	basic.	Amabrophenese.
Dibromaniline	$C_{12}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right\}N$	basic.	Amabrophenise.
Tribromaniline	$C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$	neutral.	Amabrophenose.
Chlorodibromaniline	$C_{12}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right\}N$	neutral.	Amachlobrophenose.
Nitraniline	$C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N$	basic.	Amanitrophenese.
Nitrodibromaniline	$C_{12}\left\{\begin{matrix}H_4\\Br_2\\NO_4\end{matrix}\right\}N$	neutral.	Amanitrobrophenose.

It may here be mentioned, that although, in order to include the water of the hydrated acids, I have adopted $C_{12}\,H_8$ as the nucleus of these compounds, we may also refer them to $C_{12}\,H_6$ =phène or benzine. The oxide of phenyle and the different acids will then be represented as anhydrous, thus, $C_{12}\left\{\begin{matrix}H_5\\O\end{matrix}\right.$ oxide of phenyle, &c. Aniline will be $C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right. = C_{12}\left\{\begin{matrix}H_5\\Ad\end{matrix}\right.$ =phenylamide; and chloraniline will be $C_{12}\left\{\begin{matrix}H_4\\Cl\\Ad\end{matrix}\right.$; and so on. The only compound which does not adapt itself to this formula is chloranile, $C_{12}\,Cl_4\,O_4$; which might, however, be $C_{12}\left\{\begin{matrix}Cl_3\\O_2\\ClO_2\end{matrix}\right.$, or $C_{12}\left\{\begin{matrix}Cl_2\\O_2\\2\,Cl\,O\end{matrix}\right.$.

Our space will not permit us to enter into any details concerning the preparation and properties of these interesting compounds; but it may be remarked that chloraniline by the action of hydrochloric acid and chlorate of potash yields chloranile; and that the same substance, when passed over lime (hydrated ?) at a low red heat, yields aniline, thus affording additional proof that all these compounds belong to one series, and are different subtypes of one general type. Nor must it be forgotten, that in the case of aniline, chloraniline, and bromaniline, we have chlorine and bromine substituted for hydrogen in a basic compound, without affecting its basic characters. This is the first known example of a base formed by substitution from another base, although similar facts, in regard to acids and neutral bodies, had long been known.

It is very well worthy of remark that a certain amount of chlorine or bromine, usually so antagonistic to hydrogen, does not, when substituted for that element, destroy the basic character; but that the chlorine and bromine appear to assume the function of hydrogen. A large proportion, however, of these elements, does efface the basic character.

But the existence of *nitraniline* is even more remarkable. In this body, 1 eq. of hydrogen in aniline has been replaced by 1 eq. of a powerful acid, nitrous acid, and yet the compound is decidedly basic, and retains the type of aniline.

Nitraniline forms fine golden yellow prisms, and with acids yields crystallisable salts. When acted on by bromine, it yields *nitrodibromaniline*, a neutral compound in which 2 more eqs. of hydrogen are removed and replaced by bromine.

We have here considered aniline chiefly in reference to its derivation from indigo and isatine; and the other derived bases of the same type, as also connected with indigo through chlorisatine, &c. Under the head of organic bases, a few pages further on, we shall describe more particularly the properties of aniline, and some others of its derivatives.

13. Carmine.

This name has been given to the colouring matter of cochineal which is nitrogenised, and may be obtained in dark red crystalline grains, very soluble in water and alcohol. It forms with alumina a beautiful red lake, well known as carmine. Its precise formula is not determined, but it approaches to $C_{32}H_{24}NO_{20}$.

Preisser states that the red colouring matter, like all vegetable colours, is derived by oxidation from a colourless crystalline compound which he calls *carmine.* To the red compound he gives the name of *carméine.* He has analysed neither. It may here be mentioned that Preisser has succeeded in isolating the colourless compounds (from which, as he states, the colours are derived by oxidation, especially with the aid of ammonia) in most of the red and yellow dye-stuffs, such as Brasil-wood, safflower, sandalwood, quercitron, woad, annotto, fustic, &c. He obtains them by forming lakes of the colours with oxide of lead, decomposing the lakes by sulphuretted hydrogen, which deoxidises the colouring matter, when the colourless basis is dissolved, and obtained in crystals by evaporating rapidly, or in vacuo, to avoid oxidation. He has analysed some of these compounds, but his results are not yet complete.

The finest crimson and scarlet dyes are made from cochineal, according as the mordant is alumina and tin.

Kermes is a dye stuff similar in its origin and properties to cochineal, but inferior in beauty of tint. It is derived from *Coccus ilicis.*

The red colouring matter of stick-lack, which is also used as a dye, has similar properties. Lac is produced on certain plants by the puncture of an insect.

ACTION OF NITRIC ACID ON ALOES.

This action so much resembles, in some points, the action of nitric acid on indigo, that it may be properly mentioned here. Aloes is the well-known inspissated juice of certain species of *aloe,* and is very bitter and purgative. The nature of its active principle is still unknown: but when heated with nitric acid it yields a yellow bitter substance, which is converted, by the further action of the acid, into two crystallisable acids, chrysammic and chrysolepic acid. The artificial bitter of aloes appears to be formed of two acids, aloetic and aloeretinic acids, which form red salts, but the composition of which is not exactly ascertained.

Chrysammic acid, $C_{15}HN_2O_{12}$, HO, is obtained as a yellow precipitate, when water is added to the solution obtained by heating aloes with excess of nitric acid. It is purified by being combined with potash, and this salt, after recrystallisation, is dissolved in hot water and decomposed by diluted nitric acid. The chrysammic acid is deposited as a powder formed of golden yellow shining scales. Its solution is of a fine purple. All its salts are crystallisable and of a deep red colour, frequently with green reflection, like murexide. The chrysammate of ammonia forms dark green crystals, which, when dissolved and acted on by nitric acid, deposit brilliant black scales, which are not chrysammic acid, but are transformed into it when boiled with acids or bases. The solution of chrysammate of ammonia gives with metallic salts peculiar precipitates distinct from those formed with the same salts by chrysammate of potash.

Chrysolepic acid, $C_{12} H_2 N_3 O_{13}$, HO, has the formula and many of the properties of picric acid; but is said by Schunk, who discovered it, to be different. It is darker in colour, and its salt with potash is much more soluble than picrate of potash. It would, however, appear that the two acids are essentially the same; for their salts are in general very similar, and all explode when heated. Now that picric acid is recognised as so frequent a product of the action of nitric acid, we have no difficulty in understanding its occurrence here.

ALKALOIDS OR ORGANIC BASES.

These names are given to a class of nitrogenised organic compounds which, in their relations, are quite analogous to ammonia, or rather to oxide of ammonium. They are to be distinguished from such basic oxides as oxide of ethyle, oxide of methyle, &c., which contain no nitrogen, and, although they form neutral compounds with acids, yet exist in a peculiar state in these compounds, which cannot be decomposed, like ordinary salts, by double decomposition. Thus, oxalate of oxide of ethyle does not precipitate with nitrate of lime, and chloride of ethyle does not decompose nitrate of silver. But the case is quite different with the alkaloids; for their salts undergo the same decompositions as those of ammonia.

Most of the alkaloids are found in vegetable juices, seeds, or roots; these are called vegetable alkalies, and they are generally the active principles of the plants, for the most part poisonous, in which they are found. But of late, organic bases quite analogous to those produced by nature, have been formed in a variety of processes; as, for example, the singular bases containing platinum, described at pp. 284—290; the bases containing arsenic, or arsenic and platinum, mentioned at pp. 414—418; the bases of coal tar, of which aniline, formed in several different processes, is one; the bases, chloraniline, &c., derived from aniline; the bases derived from oil of mustard, (see p. 488); those derived from the decomposition of natural alkaloids, as *quinoleine* and *cotarnine;* those formed by the action of potash on melam, as melamine and ammeline; those produced by the action of ammonia on oil of bitter almonds and analogous bodies, such as amarine, lophine, picrine, and furfurine; those formed by the action of sulphuret of ammonium on certain nitrogenised bodies, as aniline from nitrobenzide, naphthalidine from nitronaphthalese, thialdine from aldehyd-ammonia, &c.; those derived from kreatine by the action of acids and bases, namely, kreatinine and sarcosine; and such as are formed by the action of acids and bases on other animal compounds, of which glycocoll is an example, being formed from gelatine by the action of potash, and from hippuric acid by the action of hydrochloric acid. Most of these artificially formed bases are of very recent discovery, and it is evident that they must throw much light on the theory of the production of the natural alkaloids, and that the careful study of this part of the subject will, in all probability, eventually lead to the artificial formation of the natural organic bases.

The alkaloids possess, for the most part, very decided basic properties; when dissolved they act on vegetable colours like the inorganic alkalies; and they neutralise the strongest acids completely, generally forming crystallisable salts. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them at the heat of boiling water expel ammonia from its salts, owing to the volatility of the latter alkali.

Their basic properties are not derived from the oxygen they contain, for no variation in the amount of that element affects their neutralising power. On the other hand, there is every reason to believe that their basic character depends on the nitrogen they contain; for they all, without exception, contain nitrogen, although several are devoid of oxygen. Moreover, most, if not all of those which have been formed artificially, are prepared with the aid of ammonia, or some compound of ammonia, or amidogen. It is quite conceivable that they may be composed of ammonia or amidogen, *plus* some compound of carbon and hydrogen, or of carbon, hydrogen, and oxygen, the addition of which does not diminish the basic energy of the ammonia or amidogen. We shall return to this subject, after having described the alkaloids. In the mean time we shall first give an account of the natural alkaloids, and afterwards proceed to consider the artificial ones.

1. Natural Alkaloids or Vegetable Bases.

The alkaloids occur in combination, generally with vegetable acids; and they are separated from these combinations by the same means which are employed in the case of inorganic bases, modified in each case, according as the alkaloid is soluble or insoluble in water and other solvents, fixed or volatile when heated. Thus quinine, morphia, and strychnia, are separated by adding to their soluble salts, lime, ammonia, or magnesia, which form soluble salts with the acids which are present, while the alkaloids, being insoluble, are precipitated; codeine, being soluble in ether as well as water, is first set free by potash, and ether being added to the aqueous liquid, is agitated with it, and rises to the surface, carrying the codeine along with it, and the same process applies to other alkaloids. Lastly, conia, nicotine, and other volatile alkaloids are obtained by distilling their salts with an excess of liquor potassæ.

The alkaloids, like ammonia, combine with hydrogen acids forming salts, without the addition of water or its elements being necessary; they also, like ammonia, refuse to combine with anhydrous oxygen acids, requiring 1 eq. of water to form dry salts. Their hydrochlorates, like sal ammoniac, form double salts with the bichlorides of platinum and of mercury.

The salts of most of the alkaloids are precipitated as tannates by infusion of galls.

The alkaloids are generally decomposed by chlorine, bromine, and iodine, forming coloured compounds not yet fully investigated. They are also decomposed by nitric acid, some of them with a deep red colour.

Some of them, such as quinine, strychnia, &c., when heated with strong caustic potash, yield an oily compound, which is also a base, and is called quinoleine.

We shall now briefly describe the individual alkaloids, dividing them into groups, according to their characters.

a. Liquid Volatile Bases.

Nicotine, $C_{10}H_8N$. This base is found in tobacco, and is obtained by distilling the concentrated infusion of the leaves along with potash. The distilled liquid, which contains nicotine, water, and ammonia, is neutralised by sulphuric acid and the neutral solution dried up. Alcohol then dissolves the sulphate of nicotine, leaving undissolved the sulphate of ammonia. The pure sulphate, distilled with potash, yields pure nicotine, which appears as an oily, limpid, colourless liquid, having a weak smell of tobacco. Its Sp. G. is 1·048. It is decidedly alkaline, and mixes with water, alcohol, and ether. It is highly poisonous. With acids it forms salts which crystallise with difficulty. The hydrochlorate of nicotine combines with bichloride of platinum, forming a double salt, which yields large, regular, orange-red crystals, of the formula $C_{10}H_8N$,

$HCl + PtCl_2$. It is probable that nicotine, besides being found in the fresh leaves of tobacco, is produced in larger quantity during the fermentation to which the leaves are subjected in the manufacture of tobacco; and there is also reason to believe that it is produced by the action of heat on tobacco, as in smoking, and that, from the comparative simplicity of its formula, it will be found among the products of the distillation of organic compounds containing nitrogen.

Conicine. SYN. *Conia,* $C_{16} H_{16} N$? This base occurs in the hemlock, *Conium maculatum,* and is extracted by a process quite analogous to that above described for nicotine. It is also an oily liquid, boiling at 338°, highly poisonous, and easily decomposed. Its taste and smell are both very acrid and disagreeable, and somewhat analogous to those of nicotine. Its salts are acrid and poisonous, crystallising with difficulty. As it is the active principle of the conium, conicine, either pure or as a salt, ought to be used instead of the extract or tincture, which are very variable.

The two bases just described are the only natural bases belonging to the strongly marked group of volatile oily bases. But several artificial compounds are known, which belong to this group. These will be described in their proper place, and it will be seen that their analogy to nicotine and conicine is perfect.

b. Bases of Cinchona Bark.

a. Quinine. $C_{20} H_{12} N O_2$. SYN. *Chinine.* This important alkaloid is found along with cinchonine, in most species of cinchona bark. It predominates in yellow bark, *Cinchona flava, China regia,* or *C. calisaya;* and is obtained by boiling with an excess of milk of lime the decoction in diluted hydrochloric acid of the bark, and treating the precipitate with hot alcohol, which dissolves cinchonine and quinine. On evaporation, the cinchonine is deposited in crystals, and the quinine remains dissolved. Water is added, which causes the quinine to separate as a resinous mass. It may be obtained in crystals by the spontaneous evaporation of its solution in absolute alcohol. It is very sparingly soluble in water, but very soluble in alcohol and in acids. Its solutions are very bitter. When heated with hydrate of potash, it yields carbonate of potash, hydrogen gas, and *quinoline* or *leukoline,* (see that substance).

Quinine is decidedly alkaline, and neutralises the acids. Its salts, especially the sulphate, are very much used in medicine, especially as febrifuge and tonic remedies, in most cases very superior to the bark in substance. The sulphate of quinine used in medicine is a basic salt, $2\ (C_{20}\ H_{12}\ NO_2) + SO_3 + 8\ HO$. The neutral sulphate is much more soluble in water; hence, in draughts, sulphate of quinine is generally dissolved in diluted sulphuric acid. The hydrochlorate, phosphate, citrate, and ferrocyanate of quinine have also been employed in medicine.

b. Cinchonine, $C_{20}\ H_{12}\ NO$. This base predominates in the grey bark, *Cinchona condaminea*, or *C. rubiginosa*, and is also found in large quantity, as well as quinine, in red bark, *C. oblongifolia*. Its preparation has been above described. It crystallises very readily, and is not so bitter as quinine, although highly febrifuge. When heated, a considerable part is sublimed. When distilled with potash, it yields quinoline. It neutralises the acids, forming crystallisable salts, which may be substituted for those of quinine.

It is very important to observe that cinchonine only differs from quinine by 1 eq. oxygen; and although hitherto no one has succeeded in converting one into the other, little doubt can be entertained that this will be accomplished in process of time. The fact that both yield quinoline is very interesting.

c. Quinoidine. This name was given by Sertuerner to a third alkaloid, which he found in the mother liquors of the preceding. It has been shown by Liebig to be nothing else than pure quinine, in the amorphous or uncrystallisable state. The cause of its assuming the amorphous state is not yet known. It is very powerful as a remedy, and is now much used under the name of amorphous quinine.

d. Aricine, $C_{20}\ H_{12}\ NO_3$? This base was found in 1828, in a cinchona bark from Arica, in Peru, and has not since occurred. It is very similar to cinchonine, from which it differs in being soluble in ether. According to the analysis of Pelletier, it contains 1 eq. oxygen more than quinine, and 2 eq. more than cinchonine, so that the three bases may be viewed as oxides of the same radical. Aricine forms salts which are crystallisable, bitter and febrifuge.

Besides the above four, other alkaloids are said to have been found in different species of cinchona; as *pitoyine*, in the *China pitoya*, *chinovine* in the *China nova*, another alkaloid in the *China of Carthagena*, *blanquinine* in the *China blanca*, which is the bark of *Cinchona ovifolia* and *C. macrocarpa*; and *cinchovatine* in *Cinchona ovata*. This last crystallises well, and forms crystallisable salts. It has been analysed, and the results lead to the formula $C_{46}\ H_{27}\ N_2\ O_8$.

c. Bases of the Papaveraceæ.

Morphine. $C_{35}\ H_{20}\ NO_6$. This alkaloid occurs in opium, which is the inspissated juice of *Papaver somniferum.* Perhaps the easiest method of extracting it is the following. The soluble part of opium is extracted by water, and the concentrated infusion is mixed with solution of chloride of calcium, this salt being added in slight excess. On standing, especially if warmed, the mixture deposits a copious brownish-grey precipitate of mixed meconate and sulphate of lime (the morphine being in the opium partly as meconate, partly as sulphate), while hydrochlorate of morphine remains in solution with a very large proportion of dark brown colouring matter. The brown solution is evaporated till, on cooling, the hydrochlorate crystallises, forming a nearly solid mass, which is subjected to very strong pressure in flannel. A thick, viscid, nearly black mother liquor is thus expressed, which contains all the narcotine and colouring matter. The squeezed mass or cake of hydrochlorate of morphine is of a fawn colour. It is redissolved in hot water, filtered if necessary, and recrystallised, so much water being used, that on cooling a semisolid mass is obtained. This is again squeezed out, and if the squeezed cake is not quite white, it is only necessary to repeat the operation. A little animal charcoal in the second, or better still in the third, crystallisation, assists in removing the last traces of colour. The second and third mother liquids, although coloured, are not to be thrown away, but should be added to the solution of a fresh portion of opium, so that the small quantity of hydrochlorate which is retained in solution shall not be lost. In crystallising hydrochlorate of morphine, the liquid should always be acidulated with hydrochloric acid (after the animal charcoal is separated), because in this way very little indeed is retained in solution.

The purified hydrochlorate, which still contains about $\frac{1}{30}$ of codeine, is now dissolved in hot water, and supersaturated with ammonia; on cooling, the morphine is deposited as a snow-white crystalline powder, which may be crystallised by means of hot alcohol. The codeine remains in the mother liquor.

Morphine forms hard transparent brilliant crystals, almost insoluble in water, soluble in hot alcohol, insoluble in ether. It is decidedly alkaline, neutralising acids, and forming crystallisable salts. All its solutions are bitter, and act as narcotic poisons. It is coloured red by nitric acid, and brownish-red by iodic acid; it also strikes a deep blue with perchloride of iron.

The salts of morphine are much used in medicine, especially the hydrochlorate, the acetate, and the sulphate. A solution of any of these salts, of five grains to the ounce, may be administered in the same dose as tincture of opium (laudanum). The hydrochlorate or muriate is prepared as above described, and is used in the state in which it is obtained by repeated crystallisation, containing $\frac{1}{15}$ of its weight of a double hydrochlorate of morphine and codeine, which has much the same action. The acetate and sulphate are best made directly by dissolving in acetic and sulphuric acids the precipitated morphine till they are neutralised, and then evaporating. 1 lb. of good opium yields $1\frac{1}{2}$ oz. of hydrochlorate of morphine. These salts are most valuable anodynes, and do not derange the stomach nearly so much as an equivalent dose of laudanum; but they do not act so decidedly in producing sleep as in allaying pain and irritation; at least the sleep they induce does not come on so soon as in the case of laudanum. The patient, however, even when he does not sleep, feels refreshed, almost as if he had slept, and on the whole the preparations of morphine are preferred by the physician, and have, in this country at least, nearly banished the use of laudanum. The black drop contains impure citrate of morphine.

Codeine. $C_{35}\,H_{20}\,NO_5$. This alkaloid is obtained as above described, from the mother liquor of the precipitated morphine, which, being evaporated, deposits the double hydrochlorate of morphine and codeine. This salt being purified, is acted on by potash, which dissolves the morphine, while the codeine is left as a viscid mass, which soon becomes hard and crystalline. It is purified by solution in ether or in water, both of which solvents leave the morphine, which may be mixed with it, undissolved. The ethereal solution, by spontaneous evaporation, deposits it, especially if a little water be added, in fine anhydrous prisms; the aqueous solution gives large octahedral crystals, which are a hydrate, with 2 eq. of water.

Codeine is a powerful base, forming neutral salts with acids. Its solutions are bitter, and would seem to have an anodyne action on the system. But in certain circumstances they appear to excite intolerable itching of the whole skin. It is therefore possible, that the itching caused in some persons by opium, and by the commercial muriate of morphine, proceeds from codeine.

It is important to observe that, as cinchona bark contains three alkaloids differing only in the proportion of oxygen they contain, so the two principal bases of opium differ only by 1 eq. oxygen. Hitherto, however, it has been found impossible to convert codeine into morphine by oxidation, or morphine into codeine by deoxidation.

Thebaine. This base also occurs in opium. It is nearly insoluble in water, soluble in alcohol and ether. Its solutions are alkaline, and have an acrid metallic taste. It forms crystallisable salts with acids. According to Kane, its formula is $C_{25}\,H_{14}\,NO_3$.

Pseudomorphine, $C_{27}\,H_{18}\,NO_{14}$? This base is occasionally found in opium. It forms shining scales. It is sparingly soluble in water and weak alcohol, insoluble in absolute alcohol and in ether. It is readily dissolved by caustic potash or soda. It is coloured blue by perchloride of iron. It forms salts with acids, which are as yet little known.

Narceine, $C_{28}\,H_{20}\,NO_{12}$? This, which is a feeble base, also occurs in opium. It is sparingly soluble in water, soluble in alcohol, insoluble in ether. It melts at 197°. It is coloured blue by hydrochloric acid, but not by perchloride of iron. Acids dissolve it, but hardly form definite salts with it. In short, it ought rather to be described as an indifferent substance, were it not that its composition so much resembles that of the alkaloids.

Narcotine, $C_{46}\,H_{25}\,NO_{14}$. This is another weak base, found in opium in larger proportion than any other, except morphine. It may be obtained, either from the mother liquor of muriate of morphia by adding ammonia, or by digesting the insoluble part of opium in diluted acetic acid, and precipitating by ammonia. The impure narcotine is purified by solution in hot alcohol, with the aid of animal charcoal. On cooling, narcotine is deposited in crystals, which are insoluble in water and alkalies, soluble in alcohol, ether, and acids. Its salts are bitter, and crystallise with great difficulty.

The very recent researches of Liebig, Wöhler, and Blyth, have made known a series of products of decomposition derived from narcotine, when acted on by peroxide of manganese and sulphuric acid, and also by bichloride of platinum. These our space will only permit us briefly to mention.

1. *Opianic acid*, $C_{20}\,H_9\,O_{10} = C_{20}\,H_8\,O_9,\,HO$. This acid crystallises in slender prisms, and forms soluble and crystallisable salts with baryta and the oxides of lead and silver, and with oxide of ethyle. When melted, opianic acid passes into an insoluble state, its composition remaining the same.

2. *Opiammon*, $C_{40}\,H_{17}\,NO_{16}$. This compound is derived from 2 eq. opianate of ammonia by the loss of 1 eq. ammonia and 4 eq. water. It is a pale yellow powder, which, by boiling with water, is converted into opianic acid and opianate of ammonia.

3. *Xanthopenic acid.* When opiammon is acted on by alkalies, it gives off ammonia and yields opianate and xanthopenate of potash. An acid separates the xanthopenic acid as a yellow

flocculent precipitate. It forms salts of a fine yellow colour, but has not been fully examined. It contains nitrogen.

4. *Opiano-sulphurous acid,* $C_{20}\,H_8\,O_{11}\,S_2\,HO$, is formed by the action of sulphurous acid on opianic acid, and is produced by the substitution of 2 eq. sulphurous acid for 2 eq. water. It has a bitter taste and forms crystallisable salts.

5. *Sulphopianic acid,* $C_{20}\,H_8\left\{\begin{matrix}O_7\\S_2\end{matrix}\right\}, HO$. This acid is formed by the action of sulphuretted hydrogen on opianic acid, and is, in fact, opianic acid, in which 2 eq. of oxygen are replaced by 2 eq. sulphur. It is an amorphous yellow powder, which crystallises from alcohol. Its salts are soon decomposed, yielding sulphurets of the metals.

According to Wöhler, opianic acid is $(C_{20}\,H_6\,O_7, 2\,HO) + HO$; and in the two preceding acids the 2 eq. of water represented within the brackets are replaced by 2 eq. sulphurous acid and 2 eq. sulphuretted hydrogen. Opiammon, on this view, is $(C_{20}\,H_6\,O_7, 2\,HO) + (C_{20}\,H_6\,O_7, NH_3)$. He considers it probable that narcotine is a compound analogous to opiammon, and containing opianic acid.

6. *Hemipinic acid,* $C_{10}\,H_4\,O_5\,HO$. This is a product of oxidation of opianic acid. 1 eq. anhydrous opianic acid, $C_{20}\,H_8\,O_9$, *plus* 1 eq. oxygen, is $C_{20}\,H_8\,O_{10} = 2\,(C_{10}\,H_4\,O_5)$. The hemipinic acid crystallises in regular four-sided prisms. It forms insoluble salts with the oxides of lead and silver.

7. *Cotarnine,* $C_{25}\,H_{13}\,NO_6$. This is a base formed along with opianic acid. 1 eq. narcotine, $C_{46}\,H_{25}\,NO_{14}$, and 7 eq. oxygen yield 1 eq. cotarnine, $C_{25}\,H_{13}\,NO_6$ + 1 eq. opianic acid $C_{20}\,H_9\,O_{10}$ + 1 eq. carbonic acid CO_2 + 3 eq. water, $3\,HO$.

Cotarnine forms a deep yellow radiated mass, soluble in alcohol and in water. It is bitter and alkaline, and forms crystallisable double salts with the bichlorides of mercury and platinum.

8. *Humopinic acid* is a dark brown humus-like acid formed by the action of heat on narcotine. Its composition is not established with certainty, but resembles that of other similar bodies. It contains no nitrogen.

9. *Apophyllic acid.* This seems to be a product of decomposition of cotarnine. It forms crystals very like those of apophyllite and equally cleavable. When heated it yields an oily liquid, evidently quinoline. Its composition is not yet known, but it contains nitrogen.

10. *Narcogenine,* $C_{36}\,H_{19}\,NO_{10}$, is formed, along with opianic acid, when narcotine is not so far oxidised as to yield

cotarnine. 2 eq. narcotine with 5 eq. oxygen yield 2 eq. narcogenine, 1 eq. opianic acid, and 3 eq. water. It forms a crystallisable double salt with bichloride of platinum, but when separated, it is resolved into narcotine and cotarnine. 2 eq. narcogenine with 2 eq. oxygen contain the elements of 1 eq. narcotine, 1 eq. cotarnine, and 1 eq. carbonic acid.

11. *Narcotinic acid.* When narcotine is heated with potash it forms a soluble compound which contains an acid, apparently isomeric with narcotine, or differing from it only by 1 or 2 eq. water. When this acid, which is called narcotinic acid, is separated from its salts, it rapidly passes into narcotine, so that it is unknown in a separate form. Its atomic weight seems to be half that of narcotine, so that 1 eq. narcotine probably forms 2 eq. of the acid.

Such is a very brief and imperfect account of the results of the recent researches of Wöhler and of Blyth on narcotine. They are of very great importance as indicating a method which may lead to the discovery of the true constitution of the alkaloids.

Chelidonine, $C_{40} H_{20} N_3 O_6$. This alkaloid occurs in *Chelidonium majus*, along with *chelerythrine*. It is bitter, insoluble in water, and alkaline, forming crystallisable salts.

h. Chelerythrine, found in the same plant, forms a grey powder which excites violent sneezing. With acids it forms red salts, which are narcotic and poisonous.

i. Glaucine. This alkaloid occurs in the leaves and stem of *Glaucium luteum.* It may be obtained in pearly scales; its taste is bitter and acrid, and it forms salts with acids. Its composition is not yet ascertained.

k. Glaucopicrine is found in the root of the same plant. It is bitter and forms salts of a bitter and nauseous taste. Its composition is unknown.

d. Alkaloids of the Solanaceæ, the Strychneæ, and other Vegetable Families.

Hyoscyamine. This base is found in *Hyoscyamus niger* and other species of hyoscyamus. Its composition is not yet known. It is extracted from the seeds by a difficult and tedious process, and may also be obtained, although with much loss, by distillation with potash, like conieine. It is very prone to decomposition when in contact with mineral alkalies. It crystallises, when pure, in radiated groups of needles, but sometimes forms a viscid amorphous mass. When moist it has a stupefying smell like that of tobacco. It is very poisonous, causing, like conieine, tetanic spasms. It dilates the pupil powerfully. It is fusible and volatile, but is partly decomposed when distilled. It dissolves in water, alcohol, and ether. It neutralises the acids, forming crystallisable salts which are very poisonous.

Daturine. This base is obtained from the seeds of *Datura stramonium.* It is, in preparation and properties, very analogous to hyoscyamine. It is, however, less soluble in water, and crystallises in fine brilliant prisms, from its alcoholic solution. It is fusible, volatile, and very poisonous, dilating the pupil. Its salts are crystallisable and very poisonous. Its precise composition is unknown.

Stramonine. This is another crystalline compound found in *stramonium.* It is crystallisable, volatile, soluble in alcohol and ether, insoluble in water. Its nature is uncertain and its composition unknown.

Atropine, $C_{34} H_{23} NO_6$? This alkaloid is the active principle of *Atropa belladonna.* It is obtained like daturine, and being equally prone to decomposition, much is always lost. It is sparingly soluble in water and ether, more soluble in alcohol. It crystallises in white silky prisms, and sometimes forms an amorphous mass like glass. It is very bitter, acrid, and poisonous, dilating the pupil like hyoscyamine and daturine. It is fusible and volatile, and neutralises acids, forming salts which are bitter, acrid, and poisonous, and which crystallise. These salts, from their very powerful action in permanently dilating the pupil, are very well adapted for medical use, being much more uniform than the extract.

e. Solanine, $C_{84} H_{68} NO_{28}$? This alkaloid occurs in many species of *Solanum,* as in *S. nigrum, S. dulcamara,* and in the potato, *S. tuberosum.* In the latter it is found in large quantity, especially in the shoots, when the tubers have germinated in dark cellars. The shoots are extracted with dilute sulphuric acid, and the solution precipitated while hot by ammonia. The precipitate is purified by solution in alcohol. It forms a crystalline powder, very bitter and acrid, and highly poisonous, but not dilating the pupil. Its salts do not crystallise readily. There is some reason to suspect that the alkaloid of the shoots of potatoes may be distinct from that of the bittersweet, *Solanum dulcamara.*

f. Veratrine, $C_{34} H_{26} NO_6$? This alkaloid is found in *Veratrum sabadilla, V. album, &c.* It is extracted as atropine is, and is generally obtained as a crystalline powder, nearly white, very acrid and poisonous, exciting when introduced into the nostril violent and even dangerous sneezing. It is insoluble in water, but very soluble in alcohol, and may be obtained, by the spontaneous evaporation of its alcoholic solution, in prismatic crystals several lines in length. It is coloured red both by nitric and sulphuric acid.

Veratrine, in the form of tincture, and still more in that of ointment (1 drachm, or ½ drachm to 1 oz. of lard), is now much used as an external application in neuralgia and obstinate rheumatic pains. Its effects in many cases are highly beneficial. In making the ointment the veratrine should first be rubbed with a few drops of alcohol to an impalpable powder, and the lard then added. If this be not done, the gritty particles of veratrine in the ointment cause so much irritation when rubbed into the skin as to prevent its use for any length of time. We are indebted chiefly to Dr. Turnbull for our knowledge of the valuable properties of this alkaloid.

g. Sabadilline. This name has been given by Couerbe to a second crystalline body found by him along with veratrine. It is alkaline, soluble in hot water, insoluble in ether, and forms crystallisable salts with acids. Couerbe states its formula to be $C_{20}H_{13}NO_5$; but, according to Simon, it is a compound of veratrine with resin, containing also resinate of soda.

h. Colchicine. This alkaloid is similar to veratrine, for which it was formerly taken. It is found in *Colchicum autumnale*. It is crystallisable, bitter, and very poisonous. Nitric acid colours it blue or violet. It is soluble in water, alcohol, and ether. Its salts are crystallisable, bitter, acrid, and poisonous. They might probably be used in medicine advantageously, instead of the very uncertain preparations of colchicum which are at present employed. In a very small dose, colchicine causes purging and vomiting. Its composition is unknown.

i. Aconitine. This alkaloid, the composition of which is unknown, is found in *Aconitum napellus*, and, probably, also in *A. ferox* and other species. It is obtained by the usual method, but, being very prone to suffer change, much is lost. It forms a crystalline powder, or occasionally a vitreous amorphous mass. It is in the highest degree bitter, acrid, and poisonous, and is said by Geiger to dilate the pupil. On the other hand, the plant contracts the pupil and causes numbness of the part to which it is applied, and Dr. Turnbull has obtained an aconitine possessing these properties in a very high degree. Either, therefore, there are two bases in the aconite, or, as is much more probable, the aconitine of Geiger having an action different from that of the plant, is a product of decomposition, while that of Turnbull is unchanged.

Turnbull's aconitine is an invaluable remedy in the same painful diseases in which veratrine is employed. It is unfortunately obtained in small proportion, and as yet is very expensive. A cheaper and more productive method of preparing it is a very great desideratum.

k. Delphine, $C_{27}H_{19}NO_2$? This alkaloid, analogous to veratrine, is found in *stavesacre, Delphinum staphysagria.* It has only been obtained hitherto as a yellowish-white powder, not crystallised, very acrid, and poisonous. It forms neutral salts hitherto little examined. It may be used in the same affections and in the same manner as veratrine.

l. Staphisine. This is a substance found along with delphine, and said to be $C_{32}H_{23}NO_4$. It is acrid and poisonous, but is probably only a compound of delphine.

m. Emetine, $C_{37}H_{27}NO_{10}$? This is the active principle of ipecacuanha, the root of *Cephaelis ipecacuanha.* When pure, it is a white powder, alkaline, soluble in alcohol and in hot water, insoluble in ether. $\frac{1}{16}$ of a grain acts as an emetic. In a dose of from 2 to 4 grains it is poisonous. Its salts do not crystallise.

n. Chiococcine and *o. Violine* are two very similar alkaloids, found in *Chiococca ramosa* and *Viola odorata.* They are supposed by some to be emetine disguised by a little foreign matter.

p. Strychnine, $C_{44}H_{23}N_2O_8$, or $C_{44}H_{24}N_2O_8$. This alkaloid is found in nux vomica, the seeds of *Strychnos nux vomica,* in St. Ignatius's bean, the seed of *S. Ignatii,* in the wood of *S. colubrina,* and in the poison called *Upas ticuté,* derived from *S. ticuté.* It is extracted by decoction with dilute sulphuric acid, precipitating the decoction with milk of lime, and acting on the precipitate, after washing it with cold alcohol, by boiling alcohol, which on cooling deposits the strychnine in very regular transparent brilliant crystals. If brucine is present, it remains chiefly in the mother liquid, but the two bases may be separated by converting both into nitrates, and crystallising; the nitrate of strychnine crystallises readily, while the nitrate of brucine remains dissolved.

Strychnine is very insoluble, requiring 7000 parts of water. It is so bitter, that 1 part gives a very strong and persistent bitter taste to 40,000 parts of water. It dissolves in hot alcohol, although sparingly if the alcohol be pure, and is insoluble in ether. When pure, it is only coloured yellow by nitric acid; a trace of brucine causes it to be reddened by that acid. It forms crystallisable salts, which are intensely bitter. Their solutions are precipitated white by alkalies, by tincture of galls, and by iodide of potassium, in white crystals by sulphocyanide of potassium, and as yellow powders by solutions of gold and platinum.

Strychnine and its salts, especially the latter, from their solubility, are most energetic poisons. They produce spasmodic motions, and are used in very small doses as remedies in paralysis ; they seem to have a specific action on the lower part of the spinal column. The average dose is $\frac{1}{12}$ of a grain. In the event of an overdose, the best antidote is infusion of galls or strong tea, which also contains tannine.

q. Brucine, $C_{44} H_{25} N_2 O_7$. This alkaloid occurs along with strychnine in nux vomica, and also in the false angustura bark, the bark of *Brucia antidysenterica*. It is prepared as strychnine. Besides the methods above mentioned for separating the two bases, there is another, which is, to boil the mixture with water as long as it dissolves brucine, or till the strychnine is no longer reddened by nitric acid. Brucine forms large transparent crystals, which I have found to become opaque in closely stopped phials. It is very bitter and poisonous, but much less so than strychnine. It may be used for the same purposes in a rather larger dose. It is reddened strongly by nitric acid, and the red solution becomes violet on the addition of solution of tin. It is thus distinguished from strychnine and morphine. Its salts, for the most part, crystallise with facility.

r. Jervine, $C_{60} H_{45} N_2 O_5$. This alkaloid is found in white hellebore, *Veratrum album*, along with veratrine, from which it is separated easily, as it crystallises first from the alcoholic solution ; and its sulphate is also far less soluble than that of veratrine. It forms a crystalline powder, fusible, insoluble in water, soluble in alcohol, and forming with sulphuric, nitric, and hydrochloric acids, very sparingly soluble salts, so that the solution of the acetate is precipitated by these three acids.

s. Curarine. This alkaloid is obtained from the South American poison called *curari*, which is derived from some plant of the family Strychnea. It is a deadly poison when introduced into a wound, but may be swallowed with impunity. The curarine forms a yellowish amorphous bitter mass, which is more poisonous than the curari which yields it. Its salts are bitter, but do not crystallise.

t. Corydaline, $C_{34} H_{22} NO_{10}$? Found in the root of *Corydalis bulbosa* and *C. fabacea*. It forms a light grey powder, very soluble in alcohol, which deposits it in crystals. It is reddened by nitric acid, and forms crystallisable salts with acetic and sulphuric acids.

u. Carapine. Found in *Carapus guianensis*. It is a white pearly fusible powder, very bitter, soluble in water and alcohol, insoluble in ether, forming crystallisable salts with hydrochloric and acetic acids.

v. Cusparine. Found in the true angustura bark, that of

Bonplandia trifoliata or *Cusparia febrifuga.* It forms fusible octahedral crystals, sparingly soluble in water, very soluble in alcohol.

w. Daphnine occurs in the bark of *Daphne gnidium* and *D. mezereon.* It is obtained by distilling the infusion with magnesia. It is alkaline and acrid, and forms crystallisable salts with nitric and sulphuric acids, according to Vauquelin. Baer and Gmelin could not obtain it.

x. Bebeerine is the active principle of the bark of the *bebeeru* tree of Guiana, which seems to be analogous to quinine. It has not been obtained crystallised or colourless, but as a brown mass, the composition of which is not yet ascertained. Bebeerine and its salts are bitter and highly febrifuge. Dr. Douglas Maclagan and Mr. Tilley have found its composition to be the same as that of morphine, namely $C_{35} H_{20} N O_6$?

y. Sanguinarine is found in *Sanguinaria canadensis.* It forms a grey powder, which is alkaline and yields red salts. It excites sneezing, and is possibly identical with chelerythrine.

z. Azadirine, found in *Melea azadirachta,* is alkaline, forms a crystallisable salt with sulphuric acid, and is powerfully febrifuge.

aa. Capsicine is the active principle of the capsules of *Capsicum annuum* or cayenne pepper. It has a resinous aspect and a burning taste, but when quite pure may be crystallised. It forms crystallisable salts with acetic, nitric, and sulphuric acids. It is soluble in alcohol, insoluble (when pure) in ether and in water.

bb. Crotonine occurs in the seeds of *Croton tiglium,* and may be obtained from croton oil by boiling it with water and magnesia. It forms crystals, which are fusible, soluble in alcohol, insoluble in water. It forms crystallisable salts with sulphuric and phosphoric acids.

cc. Buxine occurs in Boxwood bark. It forms a bitter, brown, amorphous mass, soluble in alcohol, alkaline, and forming a crystalline sulphate. It excites sneezing.

dd. Apyrine. Found in *Cocos lapidea.* It is a white alkaline powder, forming crystalline salts with acids.

ee. Cynapine. From *Æthusa cynapium.* It is crystallisable, soluble in water and alcohol, and forms a crystalline sulphate.

ff. Cissampeline, or *Pelosine,* from Cissampelos Pareira, is a white powder, soluble in alcohol and ether; alkaline, forming soluble salts, of which the hydrochlorate crystallises.

gg. Oxyacanthine and *Berberine* are two bitter substances found in the barberry, *Berberis vulgaris.* The former is decidedly alkaline, and forms crystallisable salts. The latter is bitter, yellow, and feebly, if at all, alkaline. It crystallises, and is used in dyeing. Its formula is $C_{33}H_{18}NO_{12}$.

hh. Surinamine and *Jamaicine* are two alkaloids, found in *Geoffrœa Surinamensis* and *G. inermis*. Both are crystallisable, and form crystallisable salts; those of the latter are precipitated by tannine and corrosive sublimate.

ii. Piperine, $C_{34}H_{19}NO_6$. This compound is found in pepper, *Piper nigrum*, and *P. longum*. It is crystallisable, soluble in alcohol, very pungent. It is a feeble base, but does form salts, especially double chlorides, containing hydrochlorate of piperine.

kk. Menispermine and *Paramenispermine* are found in *Coccculus indicus*, the seed of *Menispermum cocculus*. Menispermine is white, fusible, crystallisable, and forms salts, of which the sulphate crystallises. Its formula is $C_{18}H_{12}NO_2$.

Paramenispermine has the same composition. It is less fusible, but sublimes at a high temperature. It does not appear to form definite salts. Both are insoluble in water, and soluble in alcohol; and paramenispermine is insoluble in ether.

ll. Harmaline, $C_{24}H_{13}NO$. This alkaloid occurs united with phosphoric acid in the seeds of *Peganum Harmala*. It forms brownish-yellow prisms, bitter, astringent, and acrid, very soluble in alcohol, little soluble in water or ether. It is fusible, and partly volatile. It forms, with acids, yellow crystallisable salts. By oxidising agents, harmaline is transformed into a red matter, which forms red salts with acids. The harmala red of commerce is the powder of the seeds already transformed into the phosphate of the red harmaline. It is used in dyeing, especially in giving to silk every shade of red, rose-colour, and pink. It is produced abundantly in the steppes of southern Russia, and is little known out of that country. Fritzsche states that by oxidation harmaline yields two new bases, *leucoharmine* and *chrysoharmine*, the composition of which is not given.

mm. Theobromine, $C_9H_5N_3O_2$. This is a crystalline compound, found in cacao, the seed of *Theobroma cacao*. It can hardly be called an alkaloid. It is very analogous to the next substance, caffeine.

nn. Caffeine, $C_8H_5N_2O_2$. Syn. *Théine. Guaranine.* This remarkable compound is found in *coffee*, in *tea*, in *Guarana officinalis*, or *Paullinia sorbilis*, and in *Ilex paraguayensis*. It is best obtained by adding to a decoction of tea a slight excess of acetate of lead, and evaporating to dryness the filtered liquid. The dry mass mixed with sand, is heated in the apparatus described for benzoic acid, when caffeine is obtained in crystals. Tea yields more than 1 per cent.

Caffeine forms fine white prisms, of a silky lustre, which are soluble in water, alcohol, and ether, bitter, fusible and volatile. It is a feeble base, but forms with hydrochloric acid and sulphuric acid, salts which yield very large crystals.

It is very remarkable, that caffeine should approach so nearly in composition to alloxan and alloxantine. Anhydrous alloxan, plus 1 eq. water, is $C_8 N_2 H_5 O_{11}$, and alloxantine is $C_8 N_2 H_5 O_{10}$, while caffeine is $C_8 N_2 H_5 O_2$, differing from the one by 9, from the other by 8 eq. oxygen.

We shall hereafter see how close a connection can be traced between the bile and the urine; but in the meantime it is a most striking fact, that tea, coffee, Paraguay tea, and guarana, are all used by different and distant nations for the same purpose, namely, as a refreshing and gently stimulating drink, which notoriously promotes the vital functions, while all these plants contain the very same compound, and that one allied to the bile and the urine, the chief products of the vital metamorphosis. The quantity of caffeine in tea is indeed small, but not too small to have a perceptible influence on the system. Peligot has shown that gunpowder-tea contains 6 per cent. of théine (caffeine).

By the action of nitric acid, caffeine yields a crystalline nitrogenised compound, *nitrothéine.*

Besides caffeine, or théine, tea contains 14 or 15 per cent. of caseine, and the leaves are therefore nutritious, when eaten, as they are by some oriental nations.

c. Alkaloids found in the animal organism.

Only two such bases are yet known, namely: *urea,* already described as occurring in the urine; and *kreatinine,* which Liebig has detected both in the juice of flesh and in urine, and which will be described as an artificial base, it having been first observed as a product of the action of acids on kreatine.

The following substances have been noticed as alkaloids, but are very little known: *Castine* in *Vitex agnus castus; Cicutine* in *Cicuta virosa; Chærophylline* in *Chærophyllum bulbosum; Esenbeckine* in *Esenbeckia febrifuga; Digitaline* in *Digitalis purpurea; Eupatorine* in *Eupatorium cannabinum; Euphorbine* in *Euphorbium; Convolvuline* in *Convolvulus scammonium;* and *Pereirine* in *Pereira bark.*

2. Artificial organic bases.

Within the last few years, a very considerable number of artificial organic bases have been formed, and the number is rapidly increasing. We have already briefly alluded (page 521) to the sources and mode of preparation of this class of artificial compounds, but we shall here offer a few general remarks on the subject.

All the organic bases, at least all those which are analogous to ammonia in their relation to acids, and the salts of which undergo the ordinary decompositions, contain nitrogen as an essential element. The only organic compounds ever called bases which do not contain nitrogen, are the oxides of ethyle, methyle, and other analogous radicals. But, as formerly observed, these oxides have not the above mentioned characters of ammonia, and their salts do not undergo the usual decompositions. It is true that oxide of kakodyle, which is a perfect base, contains no nitrogen; but kakodyle has all the chemical relations of a metal, and its oxide cannot be classed with the true organic bases.

Nitrogen being an essential constituent of organic bases, it is very natural that ammonia should generally be directly or indirectly concerned in their formation, when they are derived from non-azotised substances. Such is, in point of fact, very often the case. Thus, for example, bases are formed when ammonia acts on oil of bitter almonds, on furfurole, and on oil of mustard. Again, bases are very often formed by processes of reduction, that is, of deoxidation. For example, aniline, picoline, and leucoline, occur in the destructive distillation, a process of reduction; and thialdine is formed by the action of sulphuretted hydrogen, a powerful reducing agent, on aldehyd-ammonia. Here ammonia is also present; and perhaps the most powerful and successful means at our command for the production of artificial bases, is the combined action of ammonia and sulphuretted hydrogen, or, in other words, the use of sulphuret of ammonium.

Bases are obtained when sulphuret of ammonium is made to act on nitronaphtalase, nitronaphtalese, nitrobenzole, dinitrobenzole, and nitrotoluole.

In some cases, bases are formed when azotised compounds are heated with potash or with baryta. Thus, isatine, chlorisatine, &c., when heated with potash, yield aniline and chloraniline; leucoline is formed by the action of potash on quinine, &c., melamine and ammeline, when melam is boiled with potash; glycocoll is obtained by heating gelatine with potash, and sarcosine, by heating kreatine with baryta. As, in most of these cases, hydrogen gas is given off, the process is apparently one of partial oxidation, and we see therefore that reduction is not essential.

Occasionally, acids, when boiled with azotised compounds, give rise to bases. Thus, glycocoll is formed when hippuric acid is boiled with hydrochloric acid; and kreatine, when boiled with strong acids, yields the base kreatinine.

Artificial urea, already described, is produced by a spontaneous transformation of cyanate of ammonia.

Such are the modes in which artificial bases are formed, as far as we know them at present. Most of them are of very recent discovery, and it is probable that, when more extensively applied, they will yield many new bases. New methods will also be discovered, and we may hope, ere long, to solve the problem of the artificial production of the vegetable alkaloids, a class of compounds of the highest value in medicine.

Already we have formed artificially two natural bases, namely, kreatinine and urea; and although we have not yet produced quinine or morphine, yet several of the artificial bases approach very closely in composition to that class of bodies. Thus furfurine $C_{30} N_2 H_{12} O_6$ approaches to morphine $C_{35} N H_{20} O_6$. Again, we cannot yet form nicotine, $C_{10} H_8 N$, or conicine, $C_{16} H_{16} N$; but we have produced aniline, $C_{12} H_7 N$; leucoline, $C_{18} H_8 N$; toluidine, $C_{14} H_9 N$; seminaphtalidine, $C_{10} H_5 N$; and naphtalidine, $C_{20} H_9 N$; and several of these approach to nicotine and conicine as closely in properties as they do in composition.

It is important to observe, that we seem to have acquired in some degree the remarkable power possessed by the living vegetable, of causing less complex molecules to coalesce so as to give rise to those which are more complex. Thus, when oil of bitter almonds $C_{14} H_6 O_2$ is converted into amarine $C_{42} H_{18} N_2$, or picrine $C_{42} N_4 H_{12} O_{16}$, 3 eqs. must have coalesced into 1, and to yield lophine, $C_{46} H_{16} N_2$, 4 eqs. must have been used. Again, when furfurole, $C_{15} H_6 O_6$, yields furfurine $C_{30} N_2 H_{12} O_6$, 2 eqs. must have coalesced. Till the discovery of such artificial products, all those organic compounds formed by art were the results of an opposite process, namely, of the breaking down, or resolution, of more complex into less complex molecules. We could imitate Nature in her destructive processes, but not in those of a constructive character. Now, to a certain extent, we can do both. It is hardly necessary to point out the importance of the power alluded to, which may hereafter lead to the discovery of the means of artificially producing the highly complex molecules which characterise the animal kingdom. It is in this point of view that the formation of artificial bases is so interesting, and on this account we have dwelt at some length on the general nature of the processes employed to produce them.

We shall now briefly describe the artificial bases, in so far as they have not hitherto been mentioned, and we shall group them according to their properties and the sources whence they are derived.

a. Volatile oily artificial alkaloids.

Aniline $C_{12}H_7N$. SYN. *Crystalline, Benzidam, Kyanole.* This base has already been described as derived from indigo, anthranilic acid, and isatine, and as produced also by the action of bases aided by heat on nitrotoluole (protonitrobenzoëne). It is further produced, along with other bodies, when nitrobenzole (nitrobenzide) is distilled with alcohol and potash, and when the same compound is acted on by sulphuret of ammonium. Lastly, it occurs in coal tar, and in the oil obtained by the destructive distillation of animal matter.

We shall give here, in one view, the equations which explain the production of aniline, as no other compound admits of being produced in so great a variety of ways, and all these equations are instructive.

$$1.\ \underbrace{C_{14}NH_6O_3,HO}_{\text{Anthranilic acid}} = 2CO_2 + \underbrace{C_{12}H_7N}_{\text{Aniline.}}$$

$$2.\ \underbrace{C_{16}NH_5O_4}_{\text{Isatine.}} + 4(KO,HO) = 4(KO,CO_2) + \underbrace{C_{12}H_7N}_{\text{Aniline.}} + H_2$$

$$3.\ \underbrace{C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}}_{\text{Nitrotoluole.}} + 2BaO = 2(BaO,CO_2) + \underbrace{C_{12}H_7N}_{\text{Aniline.}}$$

$$4.\ \underbrace{C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}}_{\text{Nitrobenzole.}} + 6(NH_4S) = 4HO + 6NH_3 + \underbrace{C_{12}H_7N}_{\text{Aniline.}} + S_6$$

$$5.\ \underbrace{2C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}}_{\text{Nitrobenzole.}} + \underbrace{C_4H_6O_2}_{\text{Alcohol.}} + 2(KO,HO) = \underbrace{C_{12}H_5N}_{\text{Azobenzide.}} +$$

$$\underbrace{C_{12}H_7N}_{\text{Aniline.}} + 2\underbrace{C_2O_3,KO}_{\text{Oxalate of potash.}} + 4HO$$

These equations will give the reader some idea of the great variety of processes by which one organic base may be formed, and it is probable that every one of these processes may, if applied to other compounds, give rise to other bases. In fact this is already the case, as will be seen further on, with the processes No. 2, 3, and 4.

Besides the above sources of aniline there is another, namely, the destructive distillation of azotised matter. That of indigo is explained by No. 1, as anthranilic acid is probably first formed and then destroyed. But aniline is perhaps best obtained from the basic oil of coal tar. The crude oil of coal tar is well agitated with hydrochloric acid, which takes up the basic oils in an impure state. They are separated from the acid by ammonia, and consist chiefly of aniline and leucoline. The former is found in that part of the oil which, when it is rectified, passes at near 360°, and it is purified by rectification till it distils at that temperature, combining it with oxalic acid, purifying the oxalate by crystallisation, and distilling the pure salt with potash.

Aniline is a colourless oil, highly refracting, of Sp. G. 1·020. It has a burning taste, and a pleasant vinous smell when pure. It turns the delicate purple of the dahlia to green, but does not act on turmeric. A drop of it on fir-wood, moistened with hydrochloric acid, strikes a deep yellow colour. It produces a deep but fugitive purple with a solution of bleaching powder. It neutralises acids, forming salts which have a very great tendency to crystallise, hence the name *crystalline*. In combining with oxygen acids, aniline, like ammonia, takes up 1 eq. of water, but it combines directly like ammonia with hydrogen acids. Like ammonia also, its chloride forms double salts with bichloride of platinum and other analogous salts.

Nitric acid converts aniline into nitrophenisic (picric or nitropicric) acid; and by the action of chlorine, and of chlorate of potash with hydrochloric acid, it is converted into chlorophenisic and chlorophenusic acids, chloranile and trichloraniline. Bromine produces tribromaniline. These transformations prove that aniline belongs to the series of phenyle, as formerly explained. In fact, it has the composition of phenylamide, for $C_{12}H_7N = C_{12}\left\{\begin{matrix} H_5 \\ Ad \end{matrix}\right\}$ See table, p. 517.

The analogy of aniline with ammonia extends beyond what has been above stated; for as ammonia forms, under certain circumstances, such compounds as oxamide and carbamide, the latter only known in combination, so does aniline, under similar circumstances, yield analogous compounds, *oxanilide* and *carbanilide*. It even yields *formanilide*, the analogous compound to which, formamide, is not known. A compound has also been obtained in which the oxygen of carbanilide is replaced by sulphur. (Gerhardt. Hoffman.)

Hoffman has also discovered that cyanate of aniline spontaneously passes into *aniline-urea* as cyanate of ammonia does into urea.

It has already been mentioned that by heating chlorisatine, bromisatine, &c., with potash, bases and neutral compounds are obtained in which the hydrogen of aniline is replaced by chlorine and bromine, and that by the action of sulphuretted hydrogen and ammonia on dinitrobenzole, another base, nitraniline, is formed, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid. A table of these last compounds having been already given (see p. 518), we shall here give only a tabular view of the analogy between aniline and ammonia.

Ammonia in its chloride, &c.	NH_3	Aniline in its chloride, &c.	$C_{12}NH_7$
Ammonia in its sulphate, &c.	$NH_3, HO = NH_4, O$	Aniline in its sulphate, &c.	$C_{12}NH_7, HO = C_{12}NH_8, O$
Ammonia platinum salt, &c.	$NH_4Cl + PtCl_2$	Aniline platinum salt, &c.	$C_{12}NH_8, Cl + PtCl_2$
Oxamide	$NH_2, C_2O_2 = (NH_4O, C_2O_3) - 2HO$	Oxanilide	$C_{12}NH_6C_2O_2 = (C_{12}NH_8O, C_2O_3) - 2HO$
Urea	$C_2N_2H_4O_2 = (NH_4O, C_2NO)$	Aniline-urea	$C_{14}N_2'H_8O_2 = (C_{12}NH_8O, C_2NO)$

It is impossible, after considering the facts exhibited in the above table, to doubt the perfect analogy existing in all their chemical relations, between ammonia and aniline. Our space will not admit of further details concerning the remarkable derivatives of aniline here mentioned.

Picoline, $C_{12}H_7N$, is another volatile oily base, isomeric with aniline, lately discovered in coal tar by Dr. T. Anderson. It is found in the more volatile portion of the basic oil, boiling at 272°. It has no action on bleaching-liquid or on fir wood. It is a powerful base; and as it has a strong penetrating odour, it is probably identical with the *odorine* of Unverdorben, which, however, was not obtained in a state of purity. Under *Naphtaline*, we shall return to the isomerism of aniline and picoline.

Leucoline. Syn. *Quinoline*. $C_{18}H_8N$. This base is found in the least volatile portion of the basic oil of coal tar, and is also formed when quinine, cinchonine, strychnine, and thialdine are heated with potash. It has a disagreeable smell, and boils at 460°. Its Sp. G. is 1·081. It neutralises acids, forming crystallisable salts. Its refractive and dispersive power is as high as that of bisulphuret of carbon.

Toluidine. $C_{14}H_9N$. This base is formed by the action of sulphuretted hydrogen and ammonia or nitrotoluole, as aniline is from nitrobenzole. It is derived from the fundamental compound of the series, toluole, $C_{14}H_6$, as aniline is from benzole or phène, $C_{12}H_6$.

$$\underbrace{C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}}_{\text{Nitrotoluole.}} + 6\,NH_4S = 6\,NH_3 + 4\,HO + \underbrace{C_{14}H_9N}_{\text{Toluidine.}} + S_6$$

Toluidine is, in taste and smell, very similar to aniline; and, although solid and crystalline at the ordinary temperature, it melts at 104° to a highly refracting oil, which boils at 388°. It also turns fir wood yellow, with the aid of hydrochloric acid. It belongs, therefore, evidently to the class of volatile oily bases, none of which, as we have seen, contain oxygen.

With bromine, toluidine yields a crystalline body $C_{14}\left\{\begin{matrix}H_6\\Br_3\end{matrix}\right\}N$; and chlorine appears to form an analogous compound. These products correspond to tribromaniline and trichloraniline.

Let us now place together the natural and artificial oily bases, and we shall be struck with the analogy in their composition.

Nicotine	$C_{10}H_8N$	Natural oily bases.
Conicine	$C_{16}H_{16}N$	
Aniline	$C_{12}H_7N$	Artificial oily bases.
Picoline	$C_{12}H_7N$	
Toluidine	$C_{14}H_9N$	
Leucoline	$C_{18}H_8N$	

The analogy extends to the properties of these bases; for aniline is said to be poisonous, and we have seen that in all the external characters are similar.

Aniline and toluidine have been formed from the two carbohydrogens, benzole $C_{12}H_6$, and toluole, $C_{14}H_8$, by first converting them into nitrobenzole and nitrotoluole, and then treating these compounds as above explained. It is evident, therefore, that, if we had the carbohydrogens, $C_{10}H_6$ and $C_{16}H_{15}$, we might expect to be able to form nicotine and conicine.

b. Bases derived from Naphtaline.

These bases are formed in a manner quite analogous to that in which aniline is produced from benzole, and toluidine from toluole. The carbohydrogen is first converted, by the action of nitric acid, into a compound in which H is replaced by NO_4; and the new product, according to the ingenious process devised by Zinin, is dissolved in alcohol, and acted on by ammonia and sulphuretted hydrogen.

Seminaphtalidine, $C_{10}H_5N$, is obtained when nitronaphtalèse is treated by Zinin's process.

$$\underbrace{C_{20}\left\{\begin{matrix}H_6\\ 2\,NO_4\end{matrix}\right.}_{\text{Nitronaphtalèse.}} + 12\,NH_4S = 8\,HO + 12\,NH_3 + S_{12} + 2\underbrace{(C_{10}H_5N)}_{\text{Seminaphtalidine.}}$$

It forms reddish-yellow prisms, of metallic lustre, insoluble in water, soluble in alcohol and ether, and yielding crystallisable salts with acids.

Naphtalidine, $C_{20}H_9N$, is produced, in a similar way, from nitronaphtalase.

$$\underbrace{C_{20}\left\{\begin{matrix}H_7\\ NO_4\end{matrix}\right\}}_{\text{Nitronaphtalase.}} + 6\,NH_4S = 4\,HO + 6\,NH_3 + S_6 + \underbrace{C_{20}H_9N}_{\text{Naphtalidine.}}$$

It appears in the form of colourless crystals, soluble in alcohol and ether, and combines with acids, yielding crystallisable salts.

e. Bases derived from Oil of Mustard.

These bases have already been briefly described under the head of *Oil of Mustard*. They are as follows:

1. *Thiosinnamine*, $C_8H_8N_2S_2$, formed by the action of ammonia on oil of mustard.

$$\underbrace{C_8H_5NS_2}_{\text{Oil of Mustard.}} + NH_3 = \underbrace{C_8H_8N_2S_2}_{\text{Thiosinnamine.}}$$

2. *Sinnamine*, $C_8H_6N_2$ or C_4H_3N, formed when thiosinnamine is acted on by hydrated oxide of lead.

$$\underbrace{C_8H_8N_2S_2}_{\text{Thiosinnamine.}} + 2\,(PbO, HO) = 2\,PbS + 4\,HO + \underbrace{C_8H_6N_2}_{\text{Sinnamine.}}$$

3. *Sinapoline*, $C_{14}H_{12}N_2O_2$, formed when oil of mustard is acted on by baryta or oxide of lead.

$$2\underbrace{(C_8H_5NS_2)}_{\text{Oil of Mustard.}} + 6\,PbO + 2\,HO = 2\,(PbO, CO_2) + 4\,PbS +$$

$$\underbrace{C_{14}H_{12}N_2O_2}_{\text{Sinapoline.}}$$

The above equations will serve to explain the formation of these remarkable compounds, all of which, it will be seen, are produced by the action of bases, and one of which contains sulphur, an element hitherto only known to occur in one other organic base, namely, thialdine.

d. Bases derived from Aldehyde.

These bases are of recent discovery, and have been briefly mentioned under *Aldehyde.* For the convenience of the reader, we here repeat the equation which illustrates their formation.

$$3\,(\underbrace{NH_3, C_4H_4O_2}_{\text{Aldehydammonia.}}) + 6\,HS = 2\,(NH_4, S) + 6\,HO + \underbrace{C_{12}H_{13}NS_2}_{\text{Thialdine.}}$$

Selenaldine, $C_{12}H_{13}NSe_2$, is formed by a perfectly analogous process.

e. Bases derived from Melam.

These bases have been already described, p. 328; but we shall here repeat the equation, for the sake of easy reference. When melam is boiled with potash it yields two bases, *melamine* and *ammeline.*

$$\underbrace{C_{12}H_{11}O_9}_{\text{Melam.}} + 2\,(KO, HO) = \underbrace{C_6H_6N_6}_{\text{Melamine.}} + \underbrace{C_6N_5H_5O_2}_{\text{Ammeline.}} + 2\,KO.$$

f. Bases derived from Oil of Bitter Almonds.

Two of these bases have also been mentioned, p. 360, and another has since been described. We shall now, as was promised under *Amarine* and *Lophine,* give a brief account of these compounds.

Amarine, $C_{42}H_{18}N_2$, is formed from hydrobenzamide, with which it is isomeric or polymeric, by boiling the latter compound with potash. The formation of hydrobenzamide is thus explained:

$$3\,(\underbrace{C_{14}H_6O_2}_{\text{Hyduret of Benzoyle.}}) + 2\,NH_3 = 6\,HO + \underbrace{C_{42}H_{18}N_2}_{\text{Hydrobenzamide.}}$$

When hydrobenzamide, a neutral compound, is boiled with potash, a new arrangement of particles takes place, and a base is the result. It is possible that hydrobenzamide is really $= \dfrac{C_{42}H_{18}N_2}{3}$; or, if we represent $\dfrac{N}{3}$ ($\frac{1}{3}$ of N) by Az, then hydrobenzamide will be $C_{14}H_6Az_2$; that is, hyduret of benzoyle, in which O_2 is replaced by Az_2. In this case 3 eqs. of hydrobenzamide, $C_{16}H_6Az_2$, coalesce to form 1 eq. of amarine; $3\,(C_{14}H_6Az_2) = C_{42}H_{18}N_2$.

Amarine forms fine white needles, soluble in hot alcohol, insoluble in water. It has all the characters of a powerful organic base.

Lophine, $C_{46}H_{16}N_2$, is formed when hydrobenzamide is distilled. Ammonia is given off, then a fragrant oil and a mass is left, from which ether removes a substance not yet examined, leaving the lophine undissolved. Lophine is soluble in alcohol with the aid of acids, and is precipitated by ammonia. It forms fine silky crystals, which possess all the characters of a base. We cannot as yet represent its formation accurately, because the accompanying products have not yet been properly investigated; but it is evident that if hydrobenzamide be $C_{42}H_{18}N_2$, then 2 eqs. at least must be required to yield one of lophine; and if hydrobenzamide be $C_{14}H_6Az_2$, as suggested under *Amarine*, less than 4 eqs. could not furnish one of lophine.

By the action of hot nitric acid, lophine yields a yellow crystalline compound, *trinitolophyle*, the formula of which is $C_{46}\left\{\begin{matrix}H_{13}\\3\,NO_4\end{matrix}\right\}N_2$.

Picrine, Syn. *Picryle*, $C_{42}H_{15}NO_4$, is formed when the mass produced by acting on oil of bitter almonds by sulphuret of ammonium is distilled. It is one of a large number of products, not fully examined, so that its formation cannot be represented in the usual way. It must be produced, however, by the coalescence of 3 eqs. of the oil. It forms colourless octahedrons, insoluble in water. It appears to have the properties of a weak base.

By the action of nitric acid, picrine is converted into a yellow crystalline powder, *trinitropicryle*, $C_{42}\left\{\begin{matrix}H_{12}\\3\,NO_4\end{matrix}\right\}NO_4$.

The formation of the three preceding bases is very important, in reference to the views expressed in the general remarks on the artificial bases, as they are good examples of the power of building up complex molecules from such as are less complex.

g. Base derived from Furfurole.

Furfurole, $C_{15}H_6O_6$, is a volatile oil obtained by heating bran with sulphuric acid. When this oil is acted on by ammonia, it yields a crystalline compound, *furfurolamide*, analogous to hydrobenzamide. Its formula is $C_{15}NH_6O_3$.

$$\underbrace{C_{15}H_6O_6}_{\text{Furfurole.}}+NH_3=3\,HO+\underbrace{C_{15}H_6NO_3}_{\text{Furfurolamide.}}$$

Furfurine, $C_{30}H_{12}N_2O_6$, is a base, formed when furfurolamide is dissolved in hot potash, just as amarine is formed from hydrobenzamide. Here 2 eqs. of furfurolamide coalesce to form 1 eq. of the base.

Furfurine is a powerful base, soluble in hot water, and crystallisable. It expels ammonia from its salts when heated with them, and forms crystalline salts with acids. In composition it approaches nearly to several vegetable alkaloids.

h. Bases derived from Narcotine.

These bases, *Cotarnine*, $C_{25}H_{13}NO_6$, and *Narcogenine*, $C_{36}H_{19}NO_{10}$, have been already described under *Narcotine.*

i. Bases derived from Animal Products.

Glycocoll. Syn. *Sugar of gelatine.* $C_4NH_5O_4$. This remarkable compound was first obtained among the products of the decomposition of gelatine by boiling with potash or with acids. But Dessaignes has lately discovered that it is best prepared by heating hippuric acid with hydrochloric acid, when water is taken up, and benzoic acid is the only other product.

$$\underbrace{C_{18}NH_9O_6}_{\text{Hydrated hippuric acid.}} + 2HO = \underbrace{C_{14}H_6O_4}_{\text{Hydrated benzoic acid.}} + \underbrace{C_4NH_5O_4}_{\text{Hydrated glycocoll.}}$$

It forms large transparent crystals, soluble in water, and very sweet. It has the properties of a base, and neutralises acids, forming beautifully crystallised salts; but Horsford has shown that it also combines with bases and neutral bodies. By its composition, it is closely related to many different compounds, and probably plays an important part in the animal organism.

Sarcosine. $C_6NH_7O_4$. This base is formed, along with urea, when kreatine is boiled with baryta; but the urea is resolved into carbonic acid and ammonia.

$$\underbrace{C_8N_3H_{11}O_6}_{\text{Hydrated Kreatine.}} + 2BaO + 2HO = 2(BaO, CO_2) + 2NH_3 + \underbrace{C_6NH_7O_4}_{\text{Sarcosine.}}$$

Sarcosine forms right rhombic prisms, soluble in water, fusible, and volatile at a heat not much beyond 212°. It neutralises acids, and has all the characters of an alkaloid. It is isomeric with *urethane*, or *carbamate of oxide of ethyle*, and with *lactamide* or *anhydrous lactate of ammonia.*

Kreatinine. $C_8N_3H_7O_2$. This base occurs in the juice of flesh, and in urine (Liebig); but it was first observed as a product of the action of acids on kreatine. When kreatine is boiled with hydrochloric acid, 4 eqs. of water are given off, and the new base is found combined with the acid.

$$\underbrace{C_8N_3H_{11}O_6}_{\text{Kreatine.}} + HCl = 4HO + \underbrace{(C_8N_3H_7O_2 + HCl)}_{\text{Hydrochlorate of Kreatine.}}$$

Kreatinine is separated from the hydrochlorate by means of oxide of lead. It forms prisms, soluble in water and alcohol. It combines with acids, yielding crystallisable salts, and it has all the characters of a powerful organic base.

Kreatinine is important, as occurring in the animal organism. Under the urine and the juice of flesh we shall return to it. The substance discovered by Pettenkofer in urine, is, according to Liebig, a mixture of kreatinine with kreatine.

We have now gone through the artificial as well as the natural alkaloids, and the present is the proper place to say a few words concerning the constitution of this class of compounds. Of the constitution of the vegetable bases nothing certain is known; but the modes of formation of the artificial alkaloids have suggested certain views as possible or even probable.

In the first place, it may be considered very probable that all alkaloids are formed by substitution from other substances, as, for example, aniline from nitrobenzole, and toluidine from nitrotoluole.

In the next place, some of the alkaloids may be viewed as compounds of amide, as, for example, aniline, which has the composition of phenylamide,

$$C_{12}H_7N = C_{12}H_5 + NH_2.$$

The other artificial bases analogous to aniline may be regarded in the same way; leucoline as $C_{18}H_6 + NH_2$, or toluidine as $C_{14}H_7 + NH_2$; being derived, on this view, by substitution of amide either for hydrogen in the carbo-hydrogens $C_{12}H_6$, $C_{18}H_7$, and $C_{14}H_8$, or for nitrous acid in the compounds $C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$, $C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}$, and $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$. This class of alkaloids, which contain no oxygen, seem to have the simplest constitution.

But, thirdly, there is among the artificial alkaloids a substance which may be taken as the type of a somewhat more complex class, in which the hydrogen of the fundamental compound of the series has been replaced by some compound of nitrogen and oxygen. This substance is nitraniline, which is $C_{12}N_2H_6O_4 = C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N$.

Fresenius suggests that many of the natural alkaloids, containing 4 eq. of oxygen and 2 of nitrogen, may have a constitution analogous to that of nitraniline, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid. For example, strychnine, $C_{44}\,N_2\,H_{23}\,O_4$, may be $C_{44}\left\{\begin{matrix}H_{23}\\NO_4\end{matrix}\right\}N$. Quinine, menispermine, staphisaine, and delphine, may all be associated with strychnine.

Chelidonine, $C_{40}\,N_3\,H_{20}\,O_6$, may be, according to Fresenius, binitrichelidonine, $C_{40}\left\{\begin{matrix}H_{20}\\2\,NO_3\end{matrix}\right\}N$.; 2 eq. of hydrogen being replaced by 2 eq. of hyponitrous acid.

Where the alkaloid contains 2 eq. of oxygen and 2 of nitrogen, the replacing body may be deutoxide of nitrogen. Thus, caffeine, $C_8\,N_2\,H_5\,O_2$, may be nitre-caffeine, $C_8\left\{\begin{matrix}H_5\\NO_2\end{matrix}\right\}N$; and to this class would belong cinchonine and sinapoline. Urea may be added, as it may be $C_2\left\{\begin{matrix}H_4\\NO_2\end{matrix}\right\}N$.

Another class may contain protoxide of nitrogen as replacing substance. Thus, harmaline, $C_{24}\,H_{13}\,N_2\,O$, may be nitraharmaline, $C_{24}\left\{\begin{matrix}H_{13}\\NO\end{matrix}\right\}N$; and theobromine, $C_9\,H_5\,N_3\,O_2$, may be binitra-theobromine, $C_9\left\{\begin{matrix}H_5\\2\,NO\end{matrix}\right\}N$.

Lastly, hydrogen may even be supposed to be replaced by nitric acid; and, on this supposition, jervine, $C_{60}\,H_{45}\,N_2\,O_5$, might be nitrujervine, $C_{60}\left\{\begin{matrix}H_{45}\\NO_5\end{matrix}\right\}N$.

The bases above mentioned, if such be their true constitution, are derived from radicals containing no oxygen, as aniline from benzole, &c. But there are others, which are probably derived from radicals containing oxygen. Such bases are morphine, codeine, narcotine, and others. Of these, however, in this point of view so little is known, that, as Fresenius observes, it is safest, for the present, to consider them as simple alkaloids, analogous to aniline, nicotine, or sinnamine.

The views of Fresenius have a high degree of probability, and will probably aid in enabling us to discover the true nature of the alkaloids. He points out that, on his theory, various facts connected with the alkaloids are easily explained. Thus, for example, it is easy to see on his theory, that when heated with potash ammonia is not given off; and their power of saturation cannot be proportional to their amount of oxygen or of nitrogen, as it is well known not to be. On the other hand, it appears to be proportional to the amount of nitrogen which is not in the form of an oxygen compound, such as NO, NO_2,

NO_3, NO_4, or NO_5. This nitrogen generally, perhaps always, amounts to 1 eq. in 1 eq. of the base, as may be seen in Fresenius' formulæ. The simple alkaloids, such as aniline, contain only that 1 eq. of nitrogen, just as ammonia does.

It must here be remarked that the alkaloids all appear to be of the same general type with ammonia, and that, like ammonia, they unite directly with hydrogen acids, while, to combine with oxygen acids, they take up 1 eq. of water. This leads to the conclusion, that if, in the case of ammonia, there is formed a compound analogous to metals, ammonium, which unites with salt radicals, while its oxide combines with oxygen acids, the same is probably true of the alkaloids. Thus, when ammonia acts on hydrochloric acid, we have $NH_3+HCl=NH_4+Cl$, chloride of ammonium, and when aniline combines with the same acid, we may suppose the change to be analogous; $C_{12}H_7N+HCl=C_{12}H_8N+Cl$, chloride of anilium. Again, sulphate of ammonia, NH_3, HO, SO_3, is usually considered to be sulphate of oxide of ammonium, NH_4, $O+SO_3$; and so, in like manner, sulphate of aniline, $C_{12}H_7N$, HO, SO_3, is probably sulphate of oxide of anilium, $C_{12}H_8N$, $O+SO_3$. If true of one, this is probably true of all.

Such is the present state of our knowledge with regard to the alkaloids; and, although it is still very imperfect, yet it is evident that we are now making some progress in this department of science, and may hope speedily to advance much farther.

We now come to a class of compounds, very widely distributed in the vegetable kingdom, but not exhibiting the same varieties as the class hitherto described, and not characterised by the same marked properties. This is the class of neutral or indifferent non-azotised bodies, which are never poisonous, hardly even possessed of medicinal properties, and exhibit no striking chemical characters. It includes starch, gum, or mucilage, pectine or vegetable jelly, and woody fibre or lignine, with their derivatives. We can only describe them briefly.

INDIFFERENT NON-AZOTISED COMPOUNDS.

1. Starch. $C_{12}H_{10}O_{10}$.

This very important compound is universally diffused in the vegetable kingdom. It occurs in seeds, as in those of wheat and other cerealia, and also in the leguminosæ; in roots, as in the tubers of the potato; in the stem or pith of many plants, as in Sagus Rumphii; in some barks, as that of cinnamon; and in pulpy fruits, such as the apple. Finally, it is contained in the expressed juice of most vegetables, such as the carrot, in a state of suspension, being deposited on standing.

It is chiefly extracted from wheat flour (*common starch*); from potatoes (*potato starch*); from the root of *Jatropha manihot*, (*tapioca*); from that of *Maranta arundinacea* (*arrow root*); from the stem and pith of *Sagus farinifera Rumphii* (*sago*); the substances known by these different names being all essentially the same.

When flour is kneaded with water in a cloth, the water carries off the starch in suspension, and deposits it on standing, leaving behind the gluten. By a similar process starch is purified from the cellular substance and other matters mixed with it in potatoes, which are rasped, and then treated with water as above. Sago, being finally dried at a somewhat high temperature, acquires a horny and translucent appearance.

Pure starch is a snow-white powder, of a glistening aspect, which makes a crackling noise when pressed with the finger. It is composed of transparent rounded grains, the size of which varies in different plants. Those of the potato are the largest, those of the leguminosæ, as peas, are very small, and those of wheat and rice are the smallest. Starch is insoluble in cold water, alcohol, and ether; but when heated with water it first becomes viscid, and is then converted into a kind of solution, which, however, is not complete, but is rather formed by the swelling of the grains of starch into a mucilaginous mass. On cooling, the whole forms a stiff, semi-opaque jelly. If dried up, this yields a translucent mass, which softens and swells into a jelly with water, like tragacanth. The solution, or mixture of starch and water, has the remarkable property of striking a deep blue colour with free iodine. This appears to be owing not so much to a chemical or definite combination, as to the mechanical division of the iodine; there is even reason to think that the blue colour is that of iodine finely divided, adhering to the starch as a dye does to the fibres of cloth.

When starch is warmed with water, to which has been added either some infusion of malt or some diluted acid, the viscidity of the mixture disappears, and the fluid solution is no longer coloured blue by iodine. As soon as this is the case, the whole of the starch has disappeared, and has been converted into a soluble gum called *dextrine*, from its power of causing the plane of polarisation to deviate to the right. According to the proportion of malt or of acid, and the temperature employed, the change is more or less rapid; and when the action is continued the dextrine is in its turn converted into *glucose*, or grape-sugar, which from this circumstance is also called starch-sugar.

In contact with oil of vitriol, starch appears to form a compound or coupled acid, *sulphoamidic acid*. Strong nitric acid, rubbed up with potato starch, dissolves it, forming a viscid liquid, from which water precipitates a white explosive compound, called *xyloidine*. This compound has some of the properties of gumtragacanth, but it contains the elements of nitric acid, and has not yet been fully investigated. According to Pelouze, its formula is $C_6 H_4 O_4 + NO_5$; according to Ballot it is $C_{15} H_{12} NO_{16}$; but more recent researches tend to show that the formula of xyloidine is $C_{12} \left\{ \begin{matrix} H_8 \\ 2 NO_4 \end{matrix} \right\} O_{10}$; that is starch, in which 2 eqs. of hydrogen are replaced by 2 eqs. of nitrous acid. When starch is distilled with moderately-strong sulphuric acid, it yields carbonic acid, formic acid, and a pungent volatile oil, hitherto very little examined.

The blue compound of iodine and starch is best prepared by adding to the liquid filtered from the viscid paste obtained by boiling starch with water, first iodide of potassium, and then solution of chlorine, as long as it causes a blue precipitate, which is to be washed till the water passes deep blue, and dried in vacuo. Its colour is so intense as to be nearly black. It does not appear to be a compound in definite proportions. The best method of using starch as a test for iodine in mineral waters, &c., is to add to the water some starch-paste, and then a little nitric acid or chlorine. The latter is best added in the form of gas, its weight allowing it to be poured like water; while in this way we are less likely to add an excess which would destroy the blue colour. Or we may place in the bottom of a phial the liquid to be tested, adding a little oil of vitriol, and suspending from the stopper a slip of paper moistened with starch paste. After a time, if iodine be present the paper will exhibit a tinge of blue. By these tests $\frac{1}{10000}$th part of iodine in a liquid may be detected.

With bromine, starch forms an orange-yellow precipitate, which cannot be dried without decomposition.

Dextrine is best obtained by heating to about 120° a mixture of 20 parts of starch paste and 1 part of strong infusion of malt, until iodine no longer colours the mixture blue. The addition of strong alcohol now precipitates the dextrine as a thick syrup, while any sugar remains dissolved. When dried, dextrine much resembles gum, from which, however, it differs in the extreme facility with which it is converted into sugar when warmed with dilute sulphuric acid or infusion of malt, and by not yielding mucic acid when acted on by nitric acid. The composition of dextrine is the same as that of starch. In fact, dextrine is supposed by some to be the substance which is contained in the grains of starch, inclosed in an insoluble membrane, which is burst in the process of conversion of starch into dextrine, or solution of starch, by means of acids and infusion of malt. The substance present in the malt which has the property of effecting this change, is called *diastase.* It contains nitrogen.

According to other observers, the grains of starch are composed of concentric layers of one and the same substance (dextrine ?), the outer layer being insoluble in water. As starch is found to contain a small proportion of a matter analogous to wax or to caoutchouc, we may suppose that the presence of this matter in the outer layer is the cause of its insolubility, or that the whole mass of the grains is, by its means, rendered insoluble, and endowed with the property of swelling up with water to a paste or jelly. Dextrine will then be the purified, and consequently soluble, matter of starch. If the outer coat be different from the contents of the grains, it has still the same composition; for analysis shows no difference between starch, dextrine, and the insoluble matter left on the filter when starch is boiled with diluted acids.

Leiocome. This name is given to a substance having the properties of gum, which is prepared by simply roasting or torrefying starch at about 300°. It is, in fact, capable of being used instead of gum in calico-printing, and is made on the large scale. It has a yellowish-brown colour. It is probably dextrine, more or less pure, generally containing some undecomposed starch. When well made it dissolves in cold water like gum.

Inuline. $C_{24}H_{18}O_{18}$? $C_{32}H_{24}O_{24}$? $C_{24}H_{21}O_{21}$? This is a substance analogous to starch in the roots and tubers of *Inula helenium*, *Dahlia variabilis*, *Helianthus tuberosus*, and many other synantherous plants, which do not yield ordinary starch.

It is extracted from the roots by boiling water, and is deposited by the concentrated decoction as a brittle white mass, formed of crystalline grains, or as a fine powder. It is tasteless, insoluble in cold, very soluble in hot water. Diluted sulphuric acid, with the aid of heat, rapidly converts it into grape-sugar, from which, like starch, it differs only by a certain amount of the elements of water. This may be seen by the above formulæ, which represent inuline from different plants, as it exists in its compounds with oxide of lead. It would appear to differ in different vegetables, but always retaining the character of this class of bodies, namely, the presence of hydrogen and oxygen in the proportions to form water. Iodine colours it slightly brown.

Lichenine, $C_{12}H_{10}O_{10}$. This is a variety of starch found in *Lichen islandicus*, or iceland moss. It forms, when pure, a nearly colourless, tasteless mass, which swells up into a transparent jelly with cold water, and dissolves entirely in hot water. When its solution is boiled, it forms pellicles, like milk, which adhere to the vessel. Its solution is not coloured by iodine, but the jelly is rendered blue by that test. By diluted and boiling sulphuric acid it is converted into sugar; by nitric acid into oxalic and saccharic acids. It has the composition of starch.

Saponine is the name given to a variety of starch obtained from the root of *saponaria officinalis*. Its properties are little known.

2. Gum.

This name was formerly given to almost all exudations from plants. It is now limited to certain rather abundant substances, which are solid, uncrystallisable, transparent, or translucent, colourless, or nearly so, tasteless, inodorous, soluble in water, or at least softening in it, and insoluble in alcohol, ether, fat, and volatile oils. They yield mucic acid when acted on by nitric acid. They may be divided into gums which dissolve in cold water (arabine, mucilage), and gums which only swell up to a jelly (tragacanth or bassorine, cerasine, pectine). Arabine and cerasine contain oxygen and hydrogen in the proportion to form water: the other gums are nearly analagous in composition.

Arabine, or gum arabic, is found as an exudation from several species of acacia. What is called gum senegal is essentially the same. It is nearly colourless, transparent, hard, and brittle, and has a mild taste. It is very soluble in cold water, and forms a viscid mucilage, from which alcohol precipitates the gum. The diluted solution is precipitated by silicate of potash, subacetate of lead and protonitrate of mercury. When a mixture of gum, water, and sulphuric acid is kept for some time at a temperature near boiling, it is converted into grape sugar. The composition of gum is $C_{12}H_{11}O_{11}$, that is, the same as that of cane sugar, which accounts for the transformation. Arabine yields 2 or 3 per cent. of ashes, containing a good deal of lime.

Mucilage is the name given to a substance resembling gum, found in many vegetables, such as *linseed*, *althœa*, and others. It differs from arabine in being less hard when dry, and less transparent. It would appear, however, that the mucilage of althæa-root is essentially starch inclosed in cells formed of woody fibre or cellulose. The different mucilages are resolved into grape sugar by being heated with dilute sulphuric acid, and therefore may be considered as containing, like starch and arabine, water plus carbon. Since all these mucilages contain much mineral matter, the mucilage of linseed, for example, leaving 11 per cent. of ashes rich in lime, it is probable that their peculiar qualities depend on the presence of phosphate of lime or other salts of lime, disguising either starch or arabine.

Bassorine is the name given to a substance which forms the chief part of *gum tragacanth* and of *gum bassora*, and also, according to some, of *salep*, a mucilaginous substance, obtained from the bulbs of *Orchis mascula*. According to Schmidt, however, salep is really formed of swelled up grains of starch.

Pure bassorine resembles arabine in appearance, but is less transparent, and instead of dissolving in cold water, only swells up to a very great extent, forming a viscid mass. Its composition is analogous to that of arabine, and by digestion with diluted sulphuric acid, it is transformed, like salep, into grape sugar and cellulose. *Cerasine* is the name given to that part of the gum of the cherry, plum, or almond trees, which is insoluble in cold water. It is probably identical with bassorine, or with salep.

During what is called the viscous fermentation, which takes place in certain sweet vegetable juices, as that of beet-root, there is formed, along with lactic acid and mannite, a mucilaginous compound, which causes the viscidity. When dried, it has nearly the characters and composition of arabine.

Pectine is the substance which causes the juice of some pulpy fruits, as apples and pears, to coagulate or gelatinise when mixed with alcohol, by which the pectine is precipitated. When dried, it resembles gum or isinglass, and forms a jelly with water. By the action of nitric acid it yields oxalic and mucic acids. It generally yields about 8 per cent. of ashes, containing much phosphate of lime. In contact with alkalies, it is transformed into pectic acid. *Pectic acid* is easily obtained from many vegetables, as, for example, rasped carrots, by washing them well with distilled water, and then boiling 50 parts of the squeezed residue with 300 of water and 1 of potash. The pectate of potash is deposited as a jelly in the filtered liquid on cooling. Either this salt or the pectate of lime may be decomposed by diluted hydrochloric acid, which leaves the pectic acid as a jelly, which dries up into transparent laminæ, insoluble in water but very soluble in alkalies. From these solutions acids precipitate it as a jelly. In this form it is slightly soluble in boiling water, but the solution gelatinises on the addition of acids, salts, alcohol, or sugar. It is supposed not to exist ready formed in the plants, but to be produced by the action of alkalies on pectine.

The alkaline pectates, when dry, form gummy solids, soluble in water. Alcohol causes the solution to gelatinise, and even an excess of potash or soda has the same effect. The earthy and metallic pectates are gelatinous and insoluble. When dried, pectine, pectic acid, and all the pectates, assume a cellular structure, so to speak.

The jelly formed in currant juice as well as other juices by the addition of sugar, is pectine or pectic acid. The boiling of such juices probably promotes the formation of jelly; for it has been shown that when the insoluble part of unripe currants, after being washed, is boiled with water acidulated with a vegetable acid, a considerable quantity of pectine is formed, probably by a transformation of the cellular tissue.

The composition of pectic acid is not fully ascertained. According to Regnault it is $C_{12}H_8O_{11}$, or $C_{12}H_7O_{10}$, HO. According to Mulder, it is $C_{12}H_8O_{10}$. But the researches of Chodnew have led him to adopt the formula $C_{28}H_{18}O_{24}, 2HO = C_{28}H_{20}O_{26}$. In all the formulæ there is an excess of oxygen over hydrogen.

The whole subject of the mucilaginous compounds, including pectine and pectic acid, is still very obscure and requires renewed investigations.

Apiine is a substance analogous to pectine, found in parsley, *Apium graveolens*. *Glycyrrhizine* is the name given to a substance resembling both sugar and gum, which is the chief ingredient in liquorice, the juice of the root of *Glycyrrhiza glabra*. It is soluble in hot water, and gelatinises on cooling. Its taste is sweet and also acrid; but it does not, like sugar, undergo the vinous fermentation. Its formula is said to be $C_{16}H_{12}O_6$.

Sarcocolline is a gummy matter found in the sarcocolla of commerce, which is the dried juice of *Penæa mucronata*. It is soluble in alcohol and water, and has a taste both sweet and bitter. Formula $C_{22}H_{19}O_{10}$? or $C_{40}H_{32}O_{14}$?

3. Woody Fibre.

The skeleton of plants, after everything soluble in water, alcohol, ether, diluted acids, and diluted alkalies has been removed, is called woody fibre. It varies in aspect and in composition as obtained from different plants. That of box or willow, when dried, is $C_{12}H_9O_9$; that of oak is $C_{36}H_{22}O_{22}$; and that of beech is intermediate between these two. All varieties, however, may be represented as composed of carbon plus water.

Recent researches have shown that wood is composed of two parts : 1. *cellulose*, which forms the parietes of the vegetable cells; and 2. *lignine*, which fills those cells, or forms an incrustation on their walls. The latter dissolves in strong nitric acid, the former is left undissolved. Again, oil of vitriol dissolves cellulose without blackening, and it appears to convert it into dextrine, with which it agrees in composition ; while lignine separated from cellulose is said to contain $C_{35}H_{24}O_{20}$.

Linen, cotton, and paper are woody fibre, more or less pure. All these substances, and others of similar nature, but less pure, such as tow and sawdust, yield, when acted on by nitric acid, explosive compounds, analogous to that obtained from starch, already described under the name of xyloidine.

Gun cotton is best made by immersing for two minutes 1 part of clean dry cotton wool in about 10 parts of an acid composed of equal volumes of oil of vitriol, Sp. G. 1·840, and nitric acid, Sp. G. 1·510. It is then gently pressed, to expel as much as possible of the acid, rapidly washed with water, till the water runs off tasteless, and dried by a gentle water heat. 100 parts of dry cotton are found, when thus treated, although little changed in appearance, to have increased in weight to 169·5 parts. Of this weight 102·5 parts are nitric acid, and 67, or two-thirds, of the original weight, are derived from the cotton, and represent what may be called anhydrous cotton, the remaining one-third, or 33 parts, having been lost in the shape of water, which has combined with the acid.

According to Porret and Teschemacher, anhydrous cotton is $C_{12}H_8O_8$, and gun cotton is $C_{12}H_8O_8 + 4\,NO_5$, which corresponds to the above proportions. But the gun cotton may also be $C_{12}H_8O_{12} + 4\,NO_4$, or $C_{12}H_8O_{16} + 4\,NO_3$; while xyloidine, whether from starch or from woody fibre, is $C_{12}H_8O_8 + 2\,NO_5$, $C_{12}H_8O_{10} + 2\,NO_4$, or $C_{12}H_8O_{12} + 2\,NO_3$. This explains the superior explosive force of gun cotton, the combustion of which must be much more complete. In fact, when exploded, it leaves no visible residue.

It is not probable that gun cotton will supersede gunpowder for fire arms, as it is expensive, and its preparation is somewhat uncertain. But when well made, it explodes so rapidly that it will probably be found advantageous in the blasting of rocks.

By the continued action of acids or of hot alkalies, woody fibre yields a substance which is coloured blue by iodine. Linen, cotton, or paper, all of them different forms of woody fibre, when moistened with pretty strong sulphuric acid, are converted apparently first into dextrine, and afterwards into grape sugar. When heated with a more diluted acid, linen yields an amylaceous pulp hardly soluble in water, the composition of which is $C_{12}H_{10}O_{10}$.

When exposed to air and moisture, wood undergoes eremacausis, being slowly converted into a friable mass, which contains a larger proportion of carbon than the original wood. It would appear that the oxygen of the atmosphere combines with the hydrogen, and that carbon and oxygen are given off from the residue as carbonic acid, CO_2. As the residue is found still to consist of carbon and water, it is evident that for every equivalent of carbon removed, there are separated 2 eq. of oxygen and hydrogen, so that the proportion of carbon to water in the residue is constantly increasing. Woody fibre $C_{36}H_{22}O_{22}$ will thus yield first a residue of $C_{35}H_{20}O_{20}$; then $C_{34}H_{18}O_{18}$, $C_{33}H_{16}O_{16}$, and so on. When air is left in contact with moist wood, its oxygen is removed and replaced by an equal volume of carbonic acid. This is one chief source of the insalubrity of marshy districts; and the effect is seen still more strikingly in the case of houses which have been submerged in an inundation, which are very unwholesome as long as the wood is moist.

The tendency of wood to decay is checked or destroyed by acids and many salts, especially corrosive sublimate. Out of contact of air, moist wood putrefies, yielding a white friable residue, containing less carbon than the wood. One specimen yielded $C_{33}H_{17}O_{20}$, while the corresponding product of eremacausis above mentioned is $C_{35}H_{20}O_{20}$, and the wood $C_{36}H_{22}O_{22}$.

The composition of brown coal is analogous to that of wood partially decayed, but subjected to changes of the nature of putrefaction, as well as to eremacausis. Two specimens of brown coal yielded $C_{33}H_{21}O_{16}$ and $C_{32}H_{15}O_{9}$.

All the above products of decomposition of wood may be derived from oak wood, $C_{36}H_{22}O_{22}$, by the fixation of oxygen, and the separation of water and carbonic acid.

When the substance called mould, which contains the debris of decayed vegetable matter, is boiled with alkalies, the filtered solution deposits, on the addition of acids, a brown precipitate, which has been called ulmine, humus, humine, geine, ulmic acid, humic acid, and geic acid. It is generally admitted that this precipitate is a product of the action of the alkali on the decayed vegetable matter, and the name of humus, humine, or geine is given to the substance which is believed to yield the humic acid. But this humus has not been isolated, and is not known.

Mulder examined the precipitates obtained from a variety of different sources, decayed wood, turf, peat, mould, &c. With one exception, he found all to contain nitrogen, varying from 2·5 to 7 per cent. It is evident that these substances are vegetable matter in different stages of decay. Mulder considers these precipitates as compounds of water, or water and ammonia, with three different acids: 1. acid of mould $C_{40} H_{12} O_{14}$: 2. humic acid, $C_{40} H_{12} O_{12}$: 3. ulmic acid, $C_{40} H_{14} O_{12}$.

When sugar is boiled with diluted acids, it yields brown substances analogous to, if not identical with, these acids of Mulder.

It is important to observe the general presence of ammonia in mould, &c. This ammonia has no doubt been absorbed from the air in great part; and this will explain the favourable influence which these substances exert on vegetation. They act also in furnishing, by their slow decay, a continual supply of carbonic acid.

Crenic acid and *Apocrenic acid* are two brown extractive matters, analogous to the preceding, and derived from decaying vegetable matter, which are found in certain mineral waters. They both appear to contain nitrogen.

PRODUCTS OF THE DISTILLATION OF WOOD.

When wood is heated in close vessels, it gives rise to an immense variety of products, according to the kind of wood and to the presence or absence of resinous or oily matters. In all cases there are formed gaseous, liquid, and solid products, with a residue of charcoal.

The gases are carbonic acid, carbonic oxide, olefiant gas and marsh gas. The liquids are partly soluble in water, partly insoluble. The latter constitute the tar, and are of a semifluid consistence.

The substances soluble in water are, besides water itself, acetic acid, acetone, pyroxylic spirit (hydrate of oxide of methyle), acetate of oxide of methyle, lignone, xylite and mesite.

The oily substances, insoluble in water, are very numerous, including creosote, picamar, eupion, capnomor, &c. Along with these are the compounds which at the ordinary temperature are solid, such as paraffine, naphthaline, cedriret, pittacall, pyrène, chrysène, and pyroxanthine. The last mentioned, being very volatile, chiefly accompanies the acetic or pyroligneous acid.

1. Volatile products, soluble in water.

Acetic Acid. This is one of the chief products of the distillation of woods. Its mode of purification and its properties have been already described. As prepared from this source, it is often called pyroligneous acid. The crude or impure acid is highly antiseptic ; not only because vinegar, like most acids, is so, but also because it contains much creosote dissolved. Hence it not only preserves meat, but gives to it a powerful and agreeable smoked flavour.

Pyroxylic Spirit. This name is given to the spirituous liquid, distilled from the crude pyroligneous acid before the latter is purified. It is a mixed fluid, the chief component being hydrated oxide of methyle, which is accompanied by acetate of oxide of methyle, unless it has been rectified with quicklime, which decomposes the latter. *Lignone* is the name given to a volatile liquid, somewhat resembling alcohol, observed in pyroxylic spirit by Gmelin and Liebig. Its formula is not ascertained, since it does not, as far as we know, form definite compounds, from which its equivalent might be deduced. *Xylite* is another similar volatile liquid, which, according to Schweitzer, is $C_{12}H_{12}O_5 = 2(C_2H_3O) + (C_8H_6, O_3) = 2\,Mt\,O + Ac_2O_3$; that is a compound of 2 eq. oxide of methyle and 1 eq. of a sesquiacetylic acid. When acted on by potash, it yields a crystalline salt $C_{18}H_{15}O_7$, KO, while hydrated oxide of methyle separates. An excess of potash causes the formation of three products : *xylitic naphtha*, $C_{12}H_{12}O_3$; *xylitic oil*, $C_{12}H_9O$; and *xylitic resin*, C_8H_6O. When distilled with sulphuric acid, xylite, if moist, yields a new compound, *mesiténe*, a volatile liquid, $C_6H_6O_3$. If anhydrous, it yields, besides, another compound, *methol*, a less volatile liquid, which appears to be a carbo-hydrogen, C_4H_3 ; isomeric with acetyle, if it be not that radical. *Mesite* is another volatile ethereal liquid found in pyroxylic spirit, which, according to Schweitzer, is $C_6H_6O_2$; isomeric with acetone. He considers it as composed of oxide of methyle and oxide of acetyle, $C_2H_3O + C_4H_3O = Mt\,O + Ac\,O$. The liquid called mesite by Reichenbach would appear to be acetate of oxide of methyle, $Mt\,O + Ac\,O_3$, mixed with a more highly carbonised body, apparently composed of $C_{26}H_{25}O_{15}$. This latter is resolved by the action of lime into 3 eq. acetic acid ($C_{12}H_9O_9$), and a volatile liquid, $C_{14}H_{16}O_6$. Along with the above, another liquid appears to occur in the mesite of Reichenbach, the composition of which is $C_{21}H_{23}O_{10}$. In addition to all the liquids above mentioned, as occurring in pyroxylic spirit, acetone is frequently found.

The very great similarity in properties of so many substances, namely, hydrated oxide of methyle, acetate of oxide of methyle, lignone, xylite, mesite, and acetone, is worthy of notice. Most of these liquids have nearly the same density and boiling point; they are all inflammable, and their solubility in water is nearly equal. Hence they all occur mixed, and are with great difficulty separated, so as to obtain each in a state of purity; indeed in most of them we cannot be sure that this has yet been accomplished. It is highly probable, that, like the two first, all the rest will be found to be compounds of methyle. Our knowledge on the subject is still very limited.

The purified pyroxylic spirit, or hydrated oxide of methyle, has been already fully described, along with its chief derivatives.

2. Volatile Oily Products, insoluble or sparingly soluble in Water.

a. Creosote (from κρεας, flesh, and σωζω, I preserve). This is one of the most important products of the distillation of wood. It is found, partly dissolved, in the pyroligneous acid, partly along with other oils, in the tar. When the crude pyroligneous acid is saturated at 167° with dry sulphate of soda, an oil separates, which contains much creosote. In like manner, by the rectification of tar, an oil of tar is obtained, the heavier portions of which contain a good deal of creosote. These oils are neutralised with carbonate of potash, and the fluid thus deprived of acid is distilled with water. The distilled oil is acted on by dilute phosphoric acid to remove ammonia, and, probably, traces of oily bases, again distilled, and dissolved in aqua potassæ, Sp. G. 1·12, which dissolves the creosote, along with portions of other oils, but separates a good deal of eupion, &c. The alkaline solution is now supersaturated with dilute sulphuric acid, (after having been boiled in the air till it has become dark brown,) when the impure creosote separates. It is again rectified, and the treatment with potash, boiling, addition of sulphuric acid, and rectification repeated till the rectified oil dissolves entirely in weak potash, and this alkaline solution on being boiled acquires only a slight tinge of colour. It is then finally rectified, and is pure when it continues colourless on being kept. The tar of peat appears to be very rich in creosote, and it also occurs in coal tar. Good tar, from beech wood, is said to contain from 20 to 25 per cent.

Pure creosote is a colourless transparent liquid, of a high refractive and dispersive power, of a tolerably fluid but oily consistence. Its Sp. G. is 1·037, according to Reichenbach, its discoverer, and other chemists; but there is some discrepancy on this point, Dr. Christison having always found it as high as 1·060 and upwards. Its boiling point is 397°. It gradually becomes coloured brown when kept, unless absolutely pure. Creosote has a very strong, peculiar, persistent smell of smoke, analogous also to that of castoreum, not fetid, but unpleasant when concentrated. Its taste is burning, with a sweetish after-taste. It disorganises the skin, causing a white spot, where the cuticle soon peels off, without inflammation. When applied to the interior of the mouth and to the tongue it smarts strongly, whitening and disorganising the cuticle.

Internally it is a powerful poison, but in a small dose may be employed advantageously in some cases of vomiting and disease of the mucous membrane. It is given much diluted with water. Externally, it may be employed, either in the form of aqueous solution, of ointment, or pure, as a styptic, and is a valuble application to indolent ulcers, and to many chronic cutaneous affections. Pure creosote, applied to the hollow of a decayed tooth, so as to touch the exposed nerve, instantly relieves, in many cases, the most violent toothache. It acts apparently by coagulating the secretions, and thus forming a covering for the nerve.

Creosote dissolves in about 80 or 100 parts of water, and is exceedingly soluble in alcohol and in acetic acid. These solutions have the smell, taste, and antiseptic power of the creosote.

Creosote possesses a singular antiseptic power. Flesh of all kinds, if steeped for a few hours in a weak solution of creosote, becomes insusceptible of putrefaction; and the same effect is produced when the flesh is exposed to the vapour of creosote. This is the reason why the smoke of wood possesses antiseptic properties: smoked meat or fish is merely meat or fish which has absorbed the vapour of creosote from the smoke in which it has been suspended. The creosote appears to act on flesh, &c. in virtue of its remarkable power of coagulating albumen, which also accounts for its styptic action. Tongues and hams may be smoked and effectually cured by immersing them for 24 hours in a mixture of 1 part of pure creosote and 100 of water or brine; and when thus prepared, they have the delicate smoked flavour observed in reindeer tongues, as usually cured by smoking.

Owing to the difficulty of obtaining creosote quite pure, its composition is hardly ascertained with certainty. According to Deville, whose researches are the most recent, it may be regarded as the alcohol, so to speak, of the series of benzoyle. His analyses lead to the formula $C_{14} H_8 O_3 = C_{14} H_7 O_2, HO$; but I cannot ascertain whether this be the formula he adopts.

It is particularly to be noticed, that there is a very great resemblance between creosote and carbolic acid (or hydrate of phenyle, $C_{12}H_5O, HO$), a substance obtained from coal tar, and which will soon be described. So great is this resemblance, that I am almost inclined to consider creosote as a somewhat impure carbolic acid. The taste, smell, density, (according to some), boiling point, solubility in water, &c., poisonous and antiseptic action, of these two bodies, are the same. Both combine with alkalies, forming crystallisable compounds, and, what is more important, their composition in 100 parts is almost identical. The chief differences seem to be, that carbolic acid may be obtained in crystals, which, however, on contact with the air instantly liquefy and retain the liquid form, without any appreciable change of composition, apparently from the effect of a trace of moisture. Also, the salts of carbolic acid with bases are more easily formed and more permanent than those of creosote. A splinter or shaving of fir wood, dipped into carbolic acid and then into nitric or muriatic acid, becomes first blue and then brown; which does not appear to be the case with creosote. But Laurent has recently shown, that creosote, when acted on by a mixture of hydrochloric acid and chlorate of potash, yields abundance of chloranile, a character in which it agrees with carbolic acid. Both substances also yield nitropicric acid when acted on by nitric acid, although in the case of creosote this acid is accompanied by others not yet examined. These results I have myself also obtained; and it would appear, that if creosote be not carbolic acid, contaminated with some foreign matter, these two bodies are at least closely connected, and belong apparently to the same series, which is either that of benzoyle or that of phenyle. It is not improbable that creosote may be a definite compound of carbolic acid with some substance of closely allied composition, but of basic properties.

Creosote dissolves many organic substances, such as indigo, camphor, fats, essential oils, and resins, and undergoes numerous changes by the action of acids, alkalies, and other reagents, such as chlorine, potassium, and others. With oil of vitriol it is coloured purple, and appears to form a coupled acid. None of these reactions or products have been properly investigated, and we shall, therefore, not confuse the reader by a description of them, more especially as the composition of creosote itself is doubtful.

b. Picamar is the name given by Reichenbach to another oil discovered by him along with creosote in the heavy oil of tar. It is purified by a tedious process, by the aid of potash, with which it forms a crystalline compound. When pure, it is a colourless oil, of Sp. G. 1·10, of a burning and very bitter taste (hence its name from *pix* and *amarus*), and a slight smell. It boils at about 510°. It combines with alkalies, forming crystallisable salts, and may therefore be viewed as an acid in some sense, although it is quite neutral to test paper. Its composition is unknown.

c. Capnomor (from καπνος, smoke, and μοῖρα, part), is another oil, discovered by Reichenbach, in the heavy oil of tar, along with creosote and picamar. When the creosote is purified by solution of weak potash, the oil left undissolved contains a good deal of capnomor, which is purified by a tedious process. It is a limpid, colourless oil, of a high refracting power, with an aromatic odour of ginger, and a somewhat styptic after-taste. Its Sp. G. is 0·9775; it is quite neutral, and boils at 365°. With sulphuric acid it is coloured red, and yields a coupled acid. Nitric acid converts it into oxalic acid, nitropicric acid, and another crystalline substance not yet examined.

d. Eupion from εύ, fine, and πιὸν, oil or fat), is a fourth oily liquid, discovered by Reichenbach in oil of tar. Being more volatile than the rest, it is purified chiefly by rectification. When pure it is colourless, very fluid, not greasy to the feel, but less soft than water, tasteless, and of a somewhat agreeable odour, like that of some flowers, such as *narcissus*. Its Sp. G. is 0·740; and Reichenbach states that he has even obtained it so low as 0·633, being the lightest known liquid. It is volatile, boiling at 117° or lower. It is in the highest degree indifferent, resisting the action of the strongest acids and alkalies. In fact, as it is prepared from the oil of tar by rectification and the action of potash, sulphuric, and nitric acids alternately on the rectified oil, it is evident that it must resist these agents. There is good reason to believe that several, even many, different liquids have been described under this name, and that most of these are not ready formed in the tar, but products of the action of acids, &c., on the oil of tar. Reichenbach, however, by simple rectifications of the oil obtained by distilling rape oil, obtained a liquid having the characters of eupion. So much is certain, that similar liquids are formed by the action of oil of vitriol on oil of tar. The whole of the liquids called eupion are carbohydrogens, and their formula is either CH, or some multiple of this, or else one nearly approaching to such a multiple, as $C_5 H_6$, &c. It is very remarkable that some of them are very volatile, while others, apparently of the same composition, require a strong heat, from 400° to 500° for example, to boil them.

The purest varieties of eupion burn with the aid of a wick, yielding a very brilliant luminous white flame, free from smoke, and may hereafter be turned to account.

3. Solid Products of the Distillation of Wood.

a. Paraffine. This name is given (from *parum* and *affinis*, because its affinities are feeble) to a white solid volatile substance very similar to wax, discovered by Reichenbach in tar. It occurs in the last portions of the rectification of the tar, which are semisolid. It is squeezed out, and purified by one or two crystallisations in ether, which dissolves it when boiling, and deposits it on cooling in beautiful silvery scales. These, when melted, assume, on cooling, the aspect of pure white wax.

Paraffine exists in large quantity in the Rangoon petroleum, and some other bituminous mineral products. It is formed in large quantity in the distillation of wax. It melts at 110°, and distils unchanged at a high temperature. Its Sp. G. is 0·870. It burns, in a wick, with a beautiful clear white light, free from smoke, fully equal to that of the finest wax, if not superior to it. Like eupion, it is highly indifferent, and it is, like eupion, a carbo-hydrogen, containing either C H, or some multiple of it, or a near approach to such a multiple. According to Lewy, it is $C_{20} H_{21}$. It is acted on by chlorine with the aid of heat, but the reaction is not yet studied. The strongest acids and alkalies do not act on it, even with the aid of heat, if we except fuming sulphuric acid.

b. Cedriret. This is another compound discovered by Reichenbach in oil of tar. When impure creosote is dissolved in potash, and acetic acid added, an oil separates, which contains the creosote and other oils; but a certain quantity of oily matter remains dissolved in the acetate of potash. This is distilled, until what passes over causes a red precipitate in a solution of sulphate of iron. It is then collected separately, being pure cedriret. It is a volatile solid, which crystallises in a solution of sulphate of iron, forming a net-work of orange-red crystals, which dissolve in oil of vitriol with a blue colour. Much of the colour of oil of tar is probably owing to this substance.

c. Pittacal. This is yet another compound obtained by Reichenbach from the heavy oil of tar. When the heaviest portions are nearly neutralised by potash, the addition of barytic water gives rise to a deep blue colour. This belongs to pittacal, but the mode of its purification is not yet published. When pure, it is a solid, like indigo, of a very fine deep-blue colour, exhibiting on the polished surface the aspect of gold. It admits of being fixed on cloth, and would make a valuable dye-stuff. Its composition is unknown, but it appears to contain nitrogen. Its name is derived from πιττα, pitch, and καλλος, beautiful. It is a compound of very great interest, although most probably a product of decomposition of the oil of tar, and not ready formed in it. It is very desirable that it should be further investigated.

d. Pyroxanthine. This is a volatile crystalline solid, first observed by Scanlan in the crude pyroligneous spirit. When this is rectified with lime, the lime becomes dark-brown ; and when this coloured mass is acted on by hydrochloric acid, there is left undissolved a dark-brown matter, which is a mixture of pyroxanthine and a resinous matter. The mass is boiled with hot alcohol, which, on cooling, deposits the pyroxanthine in crystals, which are purified by recrystallisation. They are of an intense yellow colour, fusible, and volatile in a current of air, or with the vapour of other substances, but partly decomposed when heated alone in a dry tube. Pyroxanthine dissolves in sulphuric acid with a deep bluish-red, and in strong hydrochloric acid with a splendid purple colour, which soon passes to dark-brown. I found its composition to be very nearly $C_{21}\ H_9\ O_4$; but as it forms no definite compounds, I could not control the analysis.

Such are the chief products of the distillation of wood, as far as they are yet known. Their importance is very great, and will be still greater when they shall have been better studied, as most of them will admit of useful applications. But no doubt can be entertained that the above numerous list is far from being complete, and that more compounds remain to be discovered in tar. Indeed, there is even now good reason to believe that several or most of the substances characterising coal tar occur also, although in smaller quantity, in wood tar. Such substances are naphthaline, anthracene, and others. It is to be borne in mind that the composition of wood tar varies, according to the kind of wood, the presence or absence of oily or resinous substances, the comparative abundance of nitrogenised matter, and finally the temperature at which the distillation is carried on.

Wood coal, brown coal, or *lignite* yields, when distilled, an oil of the consistence of butter, in which creosote, paraffine, and probably eupion, are found, along with other products not yet examined.

PRODUCTS OF THE DISTILLATION OF COAL.

Coal differs from wood in several points, although it is unquestionably derived from the decay, under pressure, of woody fibre and the other substances which make up the mass of the early vegetation of which our coal-beds are the remains. Coal contains much less water, and a much larger per centage both of carbon and nitrogen, than wood. Hence it is decomposed at a higher temperature, and yields much ammonia, cyanogen, and other nitrogenised products. We shall not here dwell on ammonia and cyanogen, further than to mention that out of the aqueous products of the coal gas-works large quantities of ammonia are obtained ; and that so much hydrocyanic acid is also present, that a patent was taken out some years since for the preparation of Prussian blue from the gas liquor. We proceed to describe the chief ingredients of coal tar.

a. Carbolic acid. SYN. *Hydrated oxide of phenyle.* $C_{12} H_5 O, HO$. This remarkable acid is found in that portion of the oil of coal tar which boils between 300° and 400°. This is agitated with twice its volume of potash ley, and the aqueous solution, on the addition of an acid, yields hydrated carbolic acid (impure) as a heavy oil. It is purified by rectification with a very little solid potash.

When pure, carbolic acid generally appears as an oily liquid, colourless, and of a high refracting power, neutral to test paper, of Sp. G. 1·062 to 1·065. It has a burning taste, and the odour of creosote, to which it has a very great resemblance. In certain circumstances it forms long needle-shaped crystals, which very readily lose the solid form by exposure to the atmosphere, and which also liquefy in sealed tubes, without any obvious cause. The crystals melt at 94°, and boil at 368°. The extraordinary resemblance between carbolic acid and creosote has been noticed above ; and there can be little doubt that, if not essentially the same, they are closely connected and belong to the same series, or contain the same radical.

A splinter of pine-wood, if dipped, first in carbolic acid, and then in moderately strong nitric acid, becomes of a deep-blue, which soon passes into brown.

According to Laurent, carbolic acid is the hydrated oxide of phenyle, $C_{12} H_5$, and its formula is $(C_{12} H_5) O, HO$. This radical, phenyle, gives rise to a series of derived compounds which may be represented as follows :—

Hydrate of Phenyle, or Carbolic Acid	$C_{12} \quad H_5, O \quad + HO$
Sulphocarbolic Acid (Sulphophenic Acid)	$C_{12} \quad H_5 \quad O, HO + 2SO_3$
Chlorophenesic Acid	$C_{12} \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right\} O, HO$
Chlorophenesic Acid, identical with the Chloridoptenic Acid of Erdmann	$C_{12} \left\{ \begin{matrix} H_2 \\ Cl_3 \end{matrix} \right\} O, HO$

Chlorophenusic Acid, Chlorinised Chlorindoptenic Acid of Erdmann	$C_{12}\left\{\begin{matrix}C_{12}\\ Cl_5\end{matrix}\right\}O,HO$
Bromophenisic Acid . . .	$C_{12}\left\{\begin{matrix}H_2\\ Br_3\end{matrix}\right\}O,HO$
Nitrophenesic Acid	$C_{12}\left\{\begin{matrix}H_3\\ 2\,NO_4\end{matrix}\right\}O,HO$
Nitrophenesic Acid, identical with Nitropicric Acid . . .	$C_{12}\left\{\begin{matrix}H_2\\ 3\,NO_4\end{matrix}\right\}O,HO$
Phenylamide (Aniline) . . .	$C_{12}H_5$ Ad.

Thus the carbolic acid is connected with the derivatives of indigo, of salicyle, and other bodies, which yield nitropicric acid. This connection is also shown in the formation of chloranile, from carbolic acid, by the action of chlorate of potash and hydrochloric acid. (See under Indigo, the formation of chloranile from aniline). It is also shown, by the fact, that salicylic acid, $C_{14}H_6G_6$, when distilled alone, with lime, or with pounded glass, is resolved into carbonic acid, $2\,CO_2$, and carbolic acid, $C_{12}H_6O_2$. The action of carbolic acid, on organic compounds, is the same as that of creosote. Thus it dissolves indigo, &c., and coagulates albumen, preventing the putrefaction of animal substances.

With bases, it forms salts, some of which crystallise, but which retain an alkaline reaction. With oil of vitriol, it yields a coupled acid, sulpho-carbolic, or sulphophenic acid, which forms a soluble salt with baryta.

The formulæ in the above table illustrate the formation, by substitution, of the chlorophenesic, chlorophenisic, and chlorophenusic, of the nitrophenesic and nitrophenisic acids. It is not necessary here to do more than point out their relation to carbolic acid and phenyle. The chlorobenzide of Mitscherlich, $C_{12}H_6Cl_6$ is, according to Laurent, hydrochlorate of chlorophenise, $3\ HCl + C_{12}\left\{\begin{matrix}H_3\\ Cl_3\end{matrix}\right.$. This last body, chlorophenise, which is obtained by the action of potash on chlorobenzide, would appear to be derived by substitution, not from phenyle $C_{12}H_5$, but from benzole $C_{12}H_6$; although it may be derived also from oxide of phenyle $C_{12}\left\{\begin{matrix}H_5\\ O\end{matrix}\right.$; as may benzole itself. Chlorophenise cannot be obtained directly from hydrate of phenyle, or its derivatives: but, on the other hand, the series of benzole has an obvious relation to that of phenyle. In fact, Laurent considers benzole as in some measure the fundamental compound, or nucleus, and calls it phene $= C_{12}H_6$.

It has already been stated that nitrophenisic acid is identical with nitropicric acid. Nitrophenesic acid is somewhat similar, and forms salts which crystallise with facility, and detonate when heated. The nitrophenesate of baryta is a beautiful salt, like bichromate of potash.

b. Volatile Bases of Coal-Tar.

Besides carbolic acid, Runge found in coal-tar two other acids, *rosolic* and *brunolic acids* (of which little is known), and three basic volatile oils, *kyanol, leukol,* and *pyrrol.* The last has been litttle examined; but the recent researches of Hoffmann have confirmed Runge's statements as to the two first, which have also been identified with bases produced from different quarters, namely, aniline and quinoline or leucoline. These bases have already been fully described under the head of volatile artificial alkaloids.

That there is a relation between aniline and carbolic acid appears from their formulæ; for aniline is the amidide of carbolic acid, or *phenamide,* being thus deduced from carbolate of ammonia. $C_{12}H_5O, NH_3 = HO + C_{12}H_5, NO_2$. The relation may be better exhibited thus:—

Carbolic Acid (anhydrous), or Oxide of Phenyle $= C_{12}H_5O$
Aniline, amaphenase, or phenylamide . . $= C_{12}H_5Ad$

As another experimental proof of this relation may be mentioned that salicylamide, $C_{14}H_5O_4, NH_2 = C_{14}H_7NO_4$, which has the same composition as protonitrobenzoene and anthranilic acid, both of which yield aniline, when heated with lime gives not aniline but carbolic acid, ammonia, and probably a carbohydrogen.

It will be remembered that picoline is isomeric with aniline. Adopting Laurent's nomenclature, as explained under naphthaline, both these compounds would be called *amaphenase;* and the relation between them would be the same as between any two of the seven forms of chlonaphtese; that is, in aniline the particular molecule of hydrogen replaced by amide is different from the molecule replaced in picoline. Aniline, therefore, would be amaphenase *a,* and picoline amaphenase *b.* For the explanation of the views entertained on this and similar subjects, see *chlonaphtese.*

Of *pyrrol,* and of *rosolic* and *brunolic acids,* so little is known that we need not dwell on them.

c. Volatile Carbohydrogens in Coal Tar.

a. Naphthaline, $C_{10}H_4$, or $C_{20}H_8$. This remarkable compound occurs in all kinds of tar, but most abundantly in coal-tar, as being formed at a very high temperature. It is formed in additional quantity when any of the elements of oil of tar, such as creosote, carbolic acid, &c., or even alcohol and ether, are passed through tubes heated to a strong red-heat. It is easily obtained by re-distilling coal-tar, when the latter portions are so full of naphthaline as to be semisolid. It is well squeezed out, and purified by sublimation and crystallisation in hot alcohol. Or the oil of coal-tar is saturated with chlorine gas, which, by destroying some of the oils, allows the naphthaline to crystallise.

Pure naphthaline is colourless and volatile, and forms large tabular, transparent crystals, of a very peculiar smell, and an acrid aromatic taste. It boils at 414°, but distils easily with the vapours of water, and is dissipated, like camphor, if left exposed at the ordinary temperature.

It is acted on by chlorine and bromine, which combine with it in the first instance, and also give rise to a large number of compounds formed by substitution; and by sulphuric and nitric acids, each of which produces a number of new compounds with it. These changes have been studied with singular perseverance and remarkable sagacity, by Laurent, more especially the action of chlorine, bromine, and nitric acid. His researches have been attended with unusual success, and he may be said to have originated and established, by these researches, the now received doctrine of substitutions. I cannot hope to give even an accurate outline of all that Laurent has done in this department, because I have nowhere seen a complete account of these curious results as they now stand; but until the author himself shall publish a complete account of his researches on naphthaline, I shall place before the reader such a general account of them as may show the great importance of the subject, and some of the interesting facts already ascertained.

1. Action of Chlorine and Bromine on Naphthaline.

(It is necessary here to explain the principle of nomenclature, provisionally adopted by Laurent, especially for cases like this of substitutions, where the ordinary nomenclature is entirely inapplicable. The nomenclature of Laurent may be thought, by some, uncouth; but it is simple, systematic, and consistent with itself. Beginning with naphthaline, he gives to the compounds formed by the successive substitution of chlorine for hydrogen, names beginning with *chlo*, and ending with a syllable in which the vowels a, e, i, o, and u, are employed to designate the replacement of 1, 2, 3, 4, and 5 eq. of hydrogen. Thus, if in naphthaline, $C_{20}\ H_8$, 1 eq. of hydrogen is replaced by chlorine, we have the compound $C_{20}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right.$. This is called chlonaph*tase*. The compound $C_{20}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right.$ is chlonaph*tese*; $C_{20}\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right.$ is chlonaph*tise*, &c. The corresponding compounds of bromine are bronaph*tase*, bronaph*tese*, and bronaph*tise*. When we get as far as chlonaph*tuse* $C_{20}\left\{\begin{matrix}H_3\\Cl_5\end{matrix}\right.$ as there are no more vowels, we begin again with *a*, adding a syllable to the word. Thus $C_{20}\left\{\begin{matrix}H_2\\Cl_6\end{matrix}\right.$ is chlonaph*talase*, $C_{20}\left\{\begin{matrix}H\\Cl_7\end{matrix}\right.$ is chlonaph*talese*, and $C_{20}Cl_8$ is chlonaph*talise*, and so on with bromine. When hydrogen is replaced, partly by chlorine, partly by bromine, then the name is so constructed that the final syllable indicates the sum of the equivalents of chlorine and bromine, while both chlorine and bromine are prefixed. Thus, chlonaphtose is $C_{20}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.$; and the compound $C_{20}\left\{\begin{matrix}H_4\\Cl_3\\Br\end{matrix}\right.$ is chlor*i*bronaph*tose*; $C_{20}\left\{\begin{matrix}H_4\\Cl\\Br_3\end{matrix}\right.$ is chlor*a*bronaph*tose*. The former of these two may also be brom*a*chlonaph*tose*, and the latter brom*i*chlonaph*tose*. We shall see, hereafter, that it may be necessary to use both forms to distinguish different compounds which are isomeric. Again, where hydrogen is replaced by NO_4, we have (NO_4 being represented by X), $C_{20}\left\{\begin{matrix}H_7\\X\end{matrix}\right.$ nitronaphtase, and so forth. In like manner, if H were replaced by Ad (Ad = NH_2), we should have $C_{20}\left\{\begin{matrix}H_7\\Ad\end{matrix}\right. = C_{20}H_9N$. This would be called *amanaphtase*; and such a compound has been already described under the name of naphthalidine. It is evident that this nomenclature, although it gives rise to words of a singular aspect, is yet easily understood, and may even, in many cases, serve as well as a formula to remind us of the composition. Laurent has applied it to many other series, as we have seen in the series of phenyle, where we have chlorophenesic, chlorophenisic, and chlorophenusic acids, &c.)

When chlorine is brought in contact with naphthaline, the latter melts, and there are formed at once two compounds of chlorine and naphthaline; the chloride of naphthaline, $C_{20}H_8 + Cl_4$; and the subchloride of naphthaline $C_{20}H_8 + Cl_2$. At the same time hydrochloric acid is disengaged, arising from the action of chlorine on one of these chlorides. The former is a solid, which is best purified by solution in hot oil of petroleum, which deposits it on cooling in crystals. It may also be purified by means of boiling ether, which dissolves it to a certain extent and deposits it on cooling. Chloride of N is decomposed by heat, yielding no less than four different isomeric forms of chlonaphtese. An alcoholic solution of potash converts it into two more forms of chlonaphtese. It is also acted on by chlorine, bromine, nitric acid, and sulphuret of ammonium, yielding many new compounds.

Subchloride of N is an oily liquid, which by the action of heat is partially changed into hydrochloric acid, and one form of chlonaphtase. An alcoholic solution of potash also converts it into chlonaphtase and chloride of potassium. Chlorine converts it into two chlorides of chlonaphtase, isomeric but distinct; if the heat is too strong there is formed one kind of chlonaphtise.

When bromine is made to act on naphthaline, no bromide of N is formed, but hydrobromic acid is separated and bronaphtase is produced.

Chlonaphtase, C_{20} (H_7 Cl), is obtained by acting on subchloride of N by alcoholic solution of potash. On the addition of water, an oily liquid separates, which is purified by rectification, and is then chlonaphtase. No isomeric modification of it is yet known, but the existence of such is extremely probable. Bromine acts on it, converting it into bromide of chlorabronaphtese, $Br_4 + C_{20} H_6 Cl Br$.

Bronaphtase, C_{20} (H_7 Br), is formed by the direct action of bromine on naphthaline, care being taken to avoid excess of bromine, which would form bronaphtese, and excess of naphthaline, which would remain unchanged. Bronaphtase is a colourless oil, decomposed by chlorine and bromine. the latter converting it into bronaphtese and the products of the further action of bromine on bronaphtese. As yet only one form of bronaphtase is known.

Chlonaphtese, C_{20} (H_6 Cl_2), occurs in no less than seven different isomeric forms. These are distinguished by Laurent as modifications *a*, *c*, *ad*, *e*, *f*, *x*, and *y*, but I am not aware of the principle on which these letters are selected. *a*, *c*, *f*, and *x*, are obtained by the action of heat on the chloride of N; *ad* and *e* by boiling chloride of N with tincture of potash; and *y* by the action of chlorine on nitronaphtese. *a* and *x* are liquid, all the rest crystallise easily. The solid forms have each a different point of fusion, and the whole seven give different results when acted on by chlorine and bromine. Since, therefore, the composition of all seven is the same, we are compelled to adopt the conclusion that it is not the same 2 eq. of hydrogen which are replaced by chlorine, and that it is not indifferent which equivalents of hydrogen are thus replaced, but that, on the contrary, the properties of these compounds depend on the particular equivalents or molecules of hydrogen replaced by chlorine, and that consequently the arrangement, or relative as well as absolute position of these molecules in the compound molecule, is a matter of far greater importance (at least, in this and other analogous cases), in reference to chemical characters, than the properties of the elements, or their place in the electro-chemical arrangement.

Referring to what I have said on the subject of types, at pp. 261—266, I would here point out that naphthaline is a type, the molecule of which is made up of 20 equivalents (not single atoms, but molecules) of carbon, and 8 equivalent molecules of hydrogen; and that chlonaphtese is a subtype, in which the 20 molecules of carbon are associated, as in the fundamental type, with 8 other molecules, not all, as before, of hydrogen, but 6 of hydrogen and 2 of chlorine, a body usually considered as entirely opposed to hydrogen, chlorine being strongly negative, and hydrogen strongly positive. Yet the type remains unchanged, and we cannot help seeing that the 2 molecules of chlorine, *in virtue of their position in reference to the* 20 *of carbon*, are playing the part of 2 molecules of hydrogen.

Further, if we conceive the 8 molecules of hydrogen in the fundamental type to occupy each a fixed position, in relation to the 20 of carbon, we see from the wonderful phenomena just indicated, namely, from the existence of seven distinct forms of chlonaphtese, that, in each of these, a different pair of molecules of hydrogen has been replaced by chlorine. If the 8 molecules of hydrogen be supposed to be numbered, according to the fixed position of each in the compound molecule of the type, then we can see that in chlonaphtese *a*, the molecules 1 and 2 may be those replaced, while in *c* the molecules 6 and 7 may be those replaced by chlorine, and so on. It is easy to calculate that in this way at least 28 different isomeric forms of chlonaphtese may exist, and of these seven are already known.

Our space will not admit of details on the different forms of chlonaphtese, but I have thought it indispensable to explain the view now taken of these singular compounds, in a general way. It is evident that we may expect much light to be thrown on the obscure subject of the molecular arrangement of compounds by continued researches in the same direction. The recent progress of those departments of physics which aro most closely allied to chemistry, has established the existence of certain relations between the atomic weight and constitution of compounds and their physical properties, such as volume or density, volatility, state in regard to cohesion, solidity, fluidity, &c., and crystalline form. We now see a prospect of tracing the connection between the molecular arrangement of compound bodies and their chemical properties; and we may even hope hereafter to be enabled, simply by accurate observation of the external properties of a body, physical and chemical, to ascertain its composition and constitution; and also to predict with accuracy the properties of compounds yet unformed, the formation of which will probably become a problem, solvable by a few rules of universal application.

For the present, we have only the distant prospect of these results; but we have only assiduously to pursue the study of nature on true inductive principles, in order to be hereafter enabled to bring into order the chaos, so to speak, of interesting and important observations, the number of which is hourly increasing, while a large proportion of them have not yet found a use or an application. We must now return to the derivatives of naphthaline, which we have only space briefly to name.

Bronaphtese, C_{20} $(H_6\ Br_2)$, is easily formed by the action of bromine on naphthaline or on bronaphtase. It is a crystallisable solid, and probably corresponds to chlonaphtese, *c*. Only one bronaphtese is yet known. It forms several compounds with bromine.

Chlonaphtise, C_{20} $(H_5\ Cl_3)$, occurs in six different forms (out of 55 which are possible), *a*, *ac*, *c*, *g*, *d*, and *ad*, all of which are crystallisable solids. They are obtained in different ways: *a* by boiling with tincture of potash the oily modification of chloride of chlonaphtase; *ac* by the action of chlorine on chlonaphtese *ad*, melted; and *g* along with some of *a*, by boiling with tincture of potash the crystallised chloride of chlonaphtase; *d* by distilling the crystallised chloride of chlonaphtase; and *ad* by boiling with tincture of potash the double chloride of naphthaline and of chlonaphtase; *a* is converted by chlorine into chlonaphtose *a;* and bromine converts it into chloribronaphtose *a*.

Bronaphtise, C_{20} $(H_5\ Cl_3)$, is obtained by heating the bromide of bronaphtise, when bromine is given off. It is crystallisable. Only one form is yet known.

Chlonaphtose, C_{20} $(H_4\ Cl_4)$, occurs in four isomeric forms, *a*, *b*, *c*, and *k*, out of a very large number which are possible. They are all crystallisable. It is unnecessary to mention the methods employed to obtain them, which are analogous to those already described for chlonaphtise or chlonaphtese.

Bronaphtose, $C_{20} (H_4 Br_4)$, appears to exist in two forms, *a* and *b*, both crystallisable.

Chlonaphtuse, $C_{20} (H_3 Cl_5)$, and *Bronaphtuse*, $C_{20} (H_3 Br_5)$, are not yet known.

Chlonaphtalase, $C_{20} (H_2 Cl_6)$, is obtained by the action of chlorine on chlonaphtise *a*. It forms soft flexible prisms.

Chlonaphtalese, $C_{20} (H Cl_7)$, is not yet known.

Chlonaphtalise, $C_{20} Cl_8$, the compound in which all the hydrogen of naphthaline is replaced by chlorine, is obtained by continuing the action of chlorine on chlonaphtise *a*. It is also crystallisable. Laurent, apparently from its crystalline form, considers it to correspond with the modifications *c* of chlonaphtese and chlonaphtise; and for the same reason he considers the only chlonaphtalase known, as chlonaphtalase *a*. In the case of chlonaphtalise, if different modifications can occur, they must depend on a different principle from that which regulates the modifications of those compounds in which both chlorine and hydrogen are concerned. But until Laurent shall publish a complete account of his views, it is not easy to ascertain exactly what those views are. I suspect some error in the only account of these researches to which I could refer.

Besides the above, there are a number of compounds derived from naphthaline, in which the hydrogen is replaced by bromine and chlorine at once.

Chlorebronaphtise a, $C_{20} (H_5 Cl_2 Br)$, is a crystalline solid very similar to chlonaphtise *a*.

Chlorebronaphtose b, $C_{20} (H_4 Cl_2 Br_2)$, is obtained by the action of bromine on chlonaphtese *f*.

Chloribronaphtose a, *Bromachlonaphtose a*, and *Bromachlonaphtose b*, are three isomeric compounds. The first is obtained by the action of bromine on chlonaphtise *a*, and the bromine is, therefore, placed second in the name. The two others are both formed when chlorine acts on bronaphtese. These are the compounds alluded to at p. 265. They furnish a very beautiful proof of the truth that the position of the replaced or replacing molecule is all-important. They are all crystallisable.

Bromechlonaphtose b, $C_{20} (H_3 Cl_3 Br_2)$, is a crystalline solid obtained by boiling chloride of bromechlonaphtise with tincture of potash.

Chloribronaphtuse, $C_{20} (H_3 Cl_3 Br_2)$ is a crystalline solid, formed by the action of bromine on chloride of naphthaline.

There remain to be described some compounds, analogous to the chlorides of naphthaline, and containing consequently chlorine or bromine, in addition to the type or subtype.

Chloride of chlonaphtase, $Cl_4 + C_{20} (H_7 Cl)$, is obtained by the action of chlorine on the subchloride of naphthaline. It is the most remarkable of the whole series from the great size and beauty of its crystals. It occurs in an isomeric form as an oily liquid. When distilled, these compounds yield different forms of chlonaphtise mixed together.

Chloride of chlonaphtese, $Cl_4 + C_{20}\ (H_6\ Cl_2)$, occurs in three isomeric forms. *a* and *x* are oily liquids, derived respectively from chlonaphtese *a* and *x* by the action of chlorine. *c* is derived from chlonaphtese *c* in the same way, and is crystalline. They all yield chlonaphtose when heated, but in different forms.

Bromide of chlonaphtese, $Br_4 + C_{20}\ (H_6\ Cl_2)$, is obtained by the action of bromine on chlonaphtese *c*. It is crystalline. An excess of bromine produces at least five different compounds.

Bromide of chlorabronaphtese, $Br_4 + C_{20}\ (H_6\ Br\ Cl)$, is formed when bromine acts on chlonaphtase. It is crystalline.

Bromide of bronaphtese, $Br_4 + C_{20}\ (H_6\ Br_2)$, is formed by the action of bromine on bronaphtese. It is crystalline, and when distilled yields hydrobromic acid and bronaphtose.

Subbromide of bronaphtise, $Br_2 + C_{20}\ (H_5\ Br_3)$, is formed along with the preceding. It is also crystalline.

Bromide of bronaphtise, $Br_4 + C_{20}\ (H_5\ Br_3)$, is also a highly crystalline solid.

Subchloride of bronaphtase, $Cl_2 + C_{20}\ (H_7\ Br)$, formed by the action of chlorine on bronaphtase, crystallises in regular rhomboidal plates.

Chloride of bronaphtese, $Cl_4 + C_{20}\ (H_6\ Br_2)$ crystallises in long prisms. *Perchloride of bronaphtise*, $Cl_5 + C_{20}\ (H_5\ Br_2)$, crystallises in right prisms with rhombic base.

Chloride of bromechlonaphtise, $Cl_4 + C_{20}\ (H_5\ Br_2\ Cl)$, crystallises in oblique rhombic prisms. When boiled with tincture of potash it yields *bromechlonaphtuse*, $C_{20}\ (H_3\ Br_2\ Cl_3)$.

All the preceding compounds have been discovered, studied, analysed, and described by Laurent, besides a large additional number of derivatives of naphthaline, under the agency of chlorine and bromine, which he has not so fully examined. Those here named are sufficient to illustrate the endless variety of compounds attainable. Every subtype of the original type of naphthaline admits of numerous permutations, and where both chlorine and bromine are present, the number of possible permutations is enormously increased. In short, these remarkable researches have only made us acquainted with a very small selection of the possible products of the action of chlorine and bromine on naphthaline, *the type remaining unchanged.*

Thus the subtype chlonaphtose, $C_{20}\ (H_4\ Cl_4)$, admits of 65 isomeric modifications, all different, as does of course bronaphtose also. But these subtypes may yield the modified subtypes, chlorabronaphtose, chlorebronaphtose, chloribronaphtose, bromachlonaphtose, bromechlonaphtose, and bromichlonaphtose, and others, difficult to name, depending on the relative proportions and positions, in the molecule of the subtype, of the 4 eq. chlorine and bromine. It is easy to imagine 14 such modified subtypes, and there appears no reason why each of them, with the two subtypes, should not admit of at least 65 isomeric forms. This would give 1040 isomeric forms, all included under the two subtypes chlonaphtose and bronaphtose, or under one subtype which may be called *naphtose*, $C_{20}\ (H_4\ X_4)$. X is here put for chlorine or bromine.

2. Action of Sulphuric Acid on Naphthaline.

When naphthaline is dissolved in warm oil of vitriol to saturation, the solution, if left exposed to the air, becomes a semisolid mass of a dirty purplish colour. This, dried on a porous brick, leaves a quantity of scales, very soluble in water and alcohol, which are a mixture of two acids.

a. Hyposulphonaphthalic acid, $C_{20}\ H_8,\ S_2\ O_5 + HO$? The above mixture, being dissolved in water, is saturated with carbonate of lead, which forms insoluble sulphate of lead, and two soluble salts, one of which is soluble in alcohol and contains this acid, and yields it when decomposed by sulphuretted hydrogen. The acid forms a hard crystalline fusible mass of an acid and bitter taste. Its salts are soluble and crystallisable. Their formula is $C_{20}\ H_{16}\ S_2\ O_5,\ MO$.

b. Hyposulphonaphtic acid, $C_{11}\ H_5\ S_2\ O_6 = C_{11}\ H_4\ S_2\ O_5,\ HO$? The lead salt insoluble in alcohol contains this acid, the salts of which are soluble, bitter, and hardly crystallisable. It is possible that a third acid accompanies these two: for Faraday obtained a third salt of baryta, and Berzelius found a third salt of lead in the mother liquid of the other two. Faraday's salt, which remains with the sulphate of baryta formed in the process by the free sulphuric acid, and may be extracted by boiling water, yields about 42 per cent. of sulphate of baryta when calcined.

The vapours of anhydrous sulphuric acid, passed over fused naphthaline, form with it a red liquid. If the acid be in excess, there is formed a new acid, the *hyposulphoglutinic acid*, besides small quantities of the preceding acids; if there be excess of naphthaline there are formed two neutral bodies, *sulphonaphthaline* and *sulphonaphthalide*.

Hyposulphoglutinic acid, when pure and dry, is a hard glassy mass. When precipitated from its salts by stronger acids, it forms a viscid hydrate like turpentine. Its salts are generally soluble and do not crystallise. Its composition is unknown.

Sulphonaphthaline, $C_{20}\ H_8\ SO_2$? is a crystalline fusible solid.

Sulphonaphthalide, $C_{24}\ H_{10}\ SO_2$? is a crystalline powder not fusible at 212°.

3. Action of Nitric Acid on Naphthaline, and its Derivatives.

Nitric acid acts on naphthaline, and gives rise to a whole series of compounds in which NO_4 is substituted for hydrogen. The same principles apply here as in the action of chlorine and bromine on naphthaline. It is to Laurent that we are indebted for our knowledge of these compounds, which our space will only allow us to name.

Nitronaphtase, $C_{20}\ H_7\ X$, (X is here put for NO_4), is best formed by causing nitrous acid to pass through melted naphthaline. It is purified by means of alcohol, and forms long prisms of a sulphur-yellow colour, fusible at 110°. Chlorine decomposes it, producing chlonaphtose. Nitric acid converts it into *nitronaphtese.* By the action of sulphuretted hydrogen and ammonia, it yields, as has been already explained, a base, *naphtalidine* or *amanaphtase,* $C_{20}\ Ad\ H_7 = C_{20}\ H_9\ N$.

Naphtalase, $C_{20}\ (H_7\ O)$, is a yellow crystalline solid formed by gently heating nitronaphtase with 10 parts of lime slightly moistened. It communicates to oil of vitriol a magnificent blue colour. It is insoluble in alcohol as well as in water, otherwise it would recall pyroxanthine, which is yellow and volatile and colours sulphuric acid purple.

Nitronaphtese, $C_{20}\ (H_6\ X_2)$, forms a crystalline powder fusible at 365°, insoluble in water, very sparingly soluble in alcohol. It is converted, by the action of sulphuretted hydrogen and ammonia, into the new artificial base, *seminaphtalidine,* $= C_{10}\ H_5\ N$.

Nitronaphteise, $C_{20}\ (H_{5\frac{1}{2}}\ X_{2\frac{1}{2}})$? is a crystalline compound formed when naphthaline is added in small quantities to a large mass of hot nitric acid. Nitronaphtese is produced along with it. It is pale-yellow and very fusible, becoming liquid even in boiling alcohol. This great fusibility prevents us, notwithstanding its strange formula, from considering it as a mixture of nitronaphtese and nitronaphtise, the former of which melts at 365°, the latter at 410°, and which are very insoluble in ether, in which liquid nitronaphteise readily dissolves.

Nitronaphtise, $C_{20}\ (H_5\ X_3)$, is formed along with the preceding, and crystallises in rhomboidal plates of a pale-yellow colour, fusible at 410°.

Nitronaphtale, $C_{19} H_5 N_3 O_{11}$, is a crystalline substance, formed by the long-continued action of nitric acid on the mother liquor of all the preceding. It melts at 420°, and sometimes solidifies in an amorphous state ; a slight heat, or touching the melted substance with a point, causes it to crystallise.

Nitronaphtesic acid, $C_{16} H_{4\frac{1}{2}} N_{1\frac{1}{2}} O_4$? $C_{32} H_9 N_3 O_8$? This acid is formed when nitronaphtalese is boiled with tincture of potash, and is separated from the potash by nitric acid. When dry it is brownish-black, and forms brown salts, which are soluble and uncrystallisable. *Nitronaphtaléisic acid,* $C_{12} H_4 O_6 N_{1\frac{1}{2}}$, or $C_{24} H_8 O_{12} N_3$, is a similar acid, formed from nitronaphtaléise. *Nitronaphtisic acid* is another brown acid, formed in the same way from nitronaphtalise.

Oxide of chloroxénaphtose, $O_2 + C_{20} (H_4 Cl_2 O_2)$, is formed when nitric acid acts on crystallised chloride of chlonaphtose. It appears as a yellow crystalline solid. It is accompanied by chloranaphtisic acid, into which it is also converted by boiling with tincture of potash.

Chloranaphtisic acid, $C_{20} H_5 Cl O_6$, is formed from the preceding compound, as follows : $C_{20} H_4 Cl_2 O_4 + HO + 2 KO = K Cl + (C_{20} H_5 Cl O_6 + K O)$. It is separated from the potash by adding an acid, and forms yellow crystals, fusible at 392°. Its salts are for the most part insoluble, and exhibit the most beautiful colours, including yellow, orange, red, and carmine.

Oxide of chloroxênaphtalise, $O_2 + C_{20} Cl_6 O_2$, is obtained along with chlophtalisic acid and other compounds, when nitric acid is boiled with *chlonaphtalase,* $C_{20} H_2 Cl_6$. It forms golden scales.

Chloroxénaphtalesic acid, $C_{20} H Cl_5 O_6$, is formed when the preceding compound is acted on by potash, which at once changes it into a fine carmine-red substance, from which acids separate the new acid as a yellow crystalline powder. It forms beautiful red salts with potash and ammonia. It is formed as follows :—$C_{20} Cl_6 O_4 + HO + 2 K O = (C_{20} H Cl_5 O_6 + KO) + K Cl$.

Phtalic or *naphtalic acid,* $C_{16} H_4 O_6, 2 HO = C_{16} H_6 O_8$, is formed by the action of nitric acid on chloride of naphthaline. It forms rounded groups of lamellar crystals, and yields crystallisable salts. When distilled with lime, it yields benzole (phéne), and carbonic acid, $C_{16} H_6 O_8 = 4 C O_2 + C_{12} H_6$. When the hydrated acid is distilled, it yields the anhydrous acid in fine elastic needles.

The acid phtalate of ammonia, $C_{16} H_4 O_6, NH_4 O, HO$, when heated yields water, 4 HO, and *phtalimide,* $C_{16} H_5 NO_4$.

Phtalamide, $C_{16}H_6NO_5$, is obtained by acting on anhydrous phtalic acid by ammonia. It appears that phtalimide is acid phtalate of ammonia, minus 4 eq. water, while phtalamide is anhydrous phtalate of ammonia, $C_{16}H_4O_6 + NH_3$, minus 1 eq. water. Both are crystalline solids, and both appear to form definite compounds with oxide of silver.

Nitrophtalic acid, $C_{16}H_3NO_{10}, 2\,HO$, is derived from phtalic acid by the substitution of 1 eq. NO_4 for 1 eq. hydrogen. $C_{16}H_4O_6 - H + NO_4 = C_{16}H_3NO_{10}$. It forms beautiful pale-yellow crystals; and when gently heated, it yields the anhydrous acid in fine white needles.

Chlophtalisic acid, $C_{16}HCl_3O_6$, is formed along with the oxide of chloroxenaphtose when chlonaphtalase is boiled with nitric acid. It is crystallisable, and represents anhydrous phtalic acid, in which 3 eq. hydrogen have been replaced by 3 eq. chlorine.

To judge from the action of chlorine unaided by heat, and of nitric acid, on naphthaline, that body, $C_{20}H_8$, is composed of two carbohydrogens, $C_{16}H_4$ and C_4H_4, the latter of which is more easily altered. The former, plus 6 eq. oxygen, yields phtalic acid, $C_{16}H_4 + O_6$; and the substitution in phtalic acid of NO_4 ($=X$), for H yields nitrophtalic acid, $C_{16}\left\{\begin{matrix}H_3\\X\end{matrix}\right.$ $+O_6$.

β. *Anthracene*, $C_{30}H_{12}$. This compound, which is polymeric with naphthaline, is also found in coal-tar, and is sometimes called paranaphthaline. It melts at 356°, and distils at 392°, yielding foliated plates. When acted on by nitric acid, it gives rise to a series of compounds, in which oxygen is substituted for hydrogen, while the compounds thus formed combine with hyponitrous acid. Thus, we have

Anthracene	$C_{30}H_{12}$
Hyponitrite of Anthracenase .	$C_{30}H_{11}O + NO_3$
Bi-hyponitrite of Anthracenese .	$C_{30}H_{10}O_2 + 2NO_3$
Ter-hyponitrite of Anthracenise .	$C_{30}H_9O_3 + 3NO_3 + 3\,HO$
Hyponitrite of Anthracenose .	$C_{30}H_8O_4 + NO_3$
Hyponitrite of Anthracenuse .	$C_{30}H_7O_5 + NO_3 + HO$
Anthracenuse	$C_{30}H_7O_5$
Chloranthracenese . . .	$C_{36}H_{10}Cl_2$

The second compound of the above list is not known; but its existence is probable. In all the works to which I have access, there appear to be errors, probably of the press, in the table, which I have ventured to correct, so as to bring the formulæ into correspondence with the systematic names devised by Laurent, who discovered all these substances, on the same principle as in the case of naphthaline.

γ. *Chrysene*, C_3H or $C_{12}H_4$, is found among the last portions of the rectification of coal-tar. It is a yellow crystalline solid, insoluble in most liquids. It melts at 455°.

δ. *Pyrene*, $C_{10}H_2$ or $C_{15}H_3$, is found accompanying the preceding. It is a good deal more fusible. When acted on by nitric acid both of the above compounds yield modifications, called, by Laurent, the hyponitrites of chrysenase and of pyrenase, $C_{12}H_3O + NO_3$ and $C_{15}H_2O + NO_3$. The former, by the continued action of nitric acid, is converted into $C_{24}H_5O_3 + 2\,NO_3$, which Laurent calls *nitrite of chrysenese* (properly, of *chrysenaese?*)

When bituminous shale is distilled, it yields a thick empyreumatic oil, composed of several products. Among these is an oil apparently identical with eupion, and another very peculiar oil, called *ampeline.* This oil has neither taste nor smell, but is in some points more analogous to creosote than to any other substance. It dissolves in water, but a few drops of acid cause it to separate. Its composition is still unknown. It may possibly be a product of the action of oil of vitriol, which is used in its preparation, on some other substance.

Ampelic Acid is formed by the action of nitric acid on that part of the oil of schist which distils at 300°. It is oily, soluble in hot water, and forms very soluble salts. Its composition is not known with certainty. A similar oil, obtained from coal-tar, was found to contain $C_{14}H_6O_6$. This would be isomeric with hydrated salicylic acid.

FOSSIL RESINS, WAX, OIL, NAPHTHA, &c.

Retinite or *Retinasphalt* is a fossil resin found in lignite or wood-coal. It is fusible and combustible, and almost entirely soluble in alcohol. *Retinic acid*, $C_{21}H_9O_3$, was found by Johnston in the retinasphalt of Bovey.

Hatchetine is another fossil resin found in the lignites of Wales. It is colourless, or slightly yellow, fusible and volatile.

Scheererite is a colourless, translucent substance, of a pearly lustre, found in the Swiss lignites. Both Hatchetine and Scheererite appear to be carbohydrogens, and much resemble paraffine, not quite pure.

Middletonite is a fossil resin, found, near Leeds, in coal.

Idrialine is a remarkable solid carbohydrogen, found in the quicksilver-mines of Idria. Its composition is C_3H, or perhaps $C_{21}H_7$; it colours oil of vitriol intensely blue, forming a coupled acid. *Succisterene*, a solid body obtained by Pelletier and Walter in the distillation of amber, has the same composition, and colours sulphuric acid blue. It is, therefore, in all probability, identical with idrialine.

Ozokerite or *Fossil Wax* is found in large masses in the bituminous schist of Slamick in Moldavia. When distilled, it yields a substance like wax, and also a good deal of paraffine. Ozokerite is very fusible, and burns with a bright flame.

Fichtelite is a fusible, volatile, crystallisable solid, found in branches of pine-trees, in the peat of the turbaries in the Fichtelgebirge. It appears to have the formula $C_{20}H_{15}$, and is probably derived from essence of turpentine, $C_{20}H_{16}$.

Tekoretine, *Phylloretine*, *Xyloretine*, and *Boloretine*, are the names of four resinous compounds, found in the peat of Denmark, on the remains of pine-trees. Tekoretine and Phylloretine are both fusible, volatile, and crystallisable. The former appears to be $C_{10}H_9$, the latter C_5H_3. Xyloretine is less fusible, and is decomposed by heat. It crystallises, and its formula is said to be $C_{40}H_{33}O_4$, which only differs from that of sylvic acid by 1 eq. hydrogen. Boloretine is fusible, but does not crystallise. Its formula is $C_{40}H_{32} + 3\,HO$, but it occurs also with 5 and 6 eq. of water.

Asphaltum, *Mineral Pitch*, *Pitch of Judea*. These are the names of certain substances of similar characters, found in different parts of the world, as in Trinidad, in Hanover, and at the Dead Sea in Palestine. They all resemble pitch in aspect, and are composed of a dark-brown resin, mixed with more or less of a brilliant black matter, *asphaltene*, $C_{20}H_{16}O_3$, or of a liquid volatile oil, *petrolene*, $C_{20}H_{16}$. The former of these is probably an oxide of the latter. The different kinds of asphaltum are much used for waterproof cements, and for pavements, or roofs. *Naphteine* is a somewhat analogous substance, found in the limestones of the Maine et Loire.

Petroleum and *Naphtha*. In certain spots, in the neighbourhood of the Caspian, in Ava, at the Tegernsee in Bavaria, at Amiano in Italy, and near Neufchatel, as well as in other places, pits dug in the earth become filled with water, on which floats, more or less abundantly, an oily matter, formerly called rock-oil. The purer kinds are little coloured and very fluid, and when distilled with water, leave hardly any residue. These are called naphtha. Other kinds, as the petroleum of Rangoon in Ava, are dark-coloured and semi-solid, but become liquid at 80° or 90°. These yield by distillation, first, much naphtha, nearly colourless, and then much paraffine, which is easily purified. Naphtha, when pure, has the Sp. G. 0·755, and its formula is C_6H_5. Rectified naphtha is used for the purpose of preserving potassium and sodium, which have no action on it if water be not present. In many places the native naphtha is used to give light.

Reichenbach found that coal, distilled with water, yielded a little of an oil very similar to petroleum.

All the above substances are formed by the decay or destruction of organic matter, chiefly wood. It is not altogether improbable that those kinds which, like the Rangoon petroleum, contain paraffine ready formed, may have been formed by the action of heat on beds of vegetable remains, situated pretty deep in the crust of the earth.

Soot and *Lamp-black* are produced by the imperfect combustion of organic matters. They contain much carbon, mixed, in soot, with an acid resinous matter, and with a substance analogous to humus, but containing nitrogen, and called *absoline.* Lamp-black, besides a little resin and oily matter, often contains naphthaline, which may be extracted by alcohol.

SULPHURISED AND NUTRITIOUS ANIMAL AND VEGETABLE PRINCIPLES.

ALBUMINOUS SUBSTANCES.

We have already seen that some essential oils contain a large proportion of sulphur, and it is probable that these oils are derived from the decomposition of compounds existing in the plants which contain much sulphur, but the true nature of which is not yet known. But while such compounds only occur in a few plants, there is another class of sulphurised compounds which occur in all plants without exception. These compounds contain nitrogen and oxygen, both in considerable proportion to the carbon and hydrogen, and a small proportion of sulphur. They are all solid, and when heated yield products containing ammonia and sulphur. They have neither a medicinal nor a poisonous action on the animal system, but are nutritious in the strict sense of the word.

Such are vegetable albumen, vegetable fibrine, and vegetable caseine, as well as animal albumen, animal fibrine, and animal caseine. The latter, when compared with the former respectively, are found to differ from them only in form, agreeing with them in all essential chemical characters. Every one of the six dissolves in strong hydrochloric acid, gently warmed, with a purple colour; and all of them likewise dissolve in caustic potash, forming a solution which, according to Mulder, yields, after boiling, on the addition of acetic acid, a gelatinous precipitate containing no sulphur, while sulphuretted hydrogen gas is disengaged. Mulder named this precipitate Proteine, believing it to be the fundamental compound in the albuminous substances, in each of which it was combined with different small proportions of sulphur, phosphorus, and salts. The following table will explain his views, proteine, according to his analysis, being $C_{40} H_{31} N_5 O_{12} = Pr.$

Crystalline humour	contains	15	eq.	Proteine	+ 1	eq.	Sulphur			
Caseine	„	10	„	„	+ 1	„	„			
Vegetable Gelatine	„	10	„	„	+ 2	„	„			
Albumen of Eggs	„	10	„	„	+ 1	„	„	+ 1	eq.	Phosphorus
Fibrine	„	10	„	„	+ 1	„	„	+ 1	„	„
Albumen of Blood	„	10	„	„	+ 2	„	„	+ 1	„	„

In this table the salts are omitted.

Mulder's view, according to which the albuminous substances are all compounds of proteine, has been generally adopted, and is at first sight very attractive, as it not only accounts for the close agreement in composition and properties among the albuminous bodies, but also enables us to perceive how they may pass into each other.

But on a closer inspection, several things appear unfavourable to the theory of proteine. In the first place: in the above table, the albumen of eggs contains less sulphur than that of blood, whereas, in fact, it contains more. Secondly: in the table, albumen of eggs and fibrine have the same formula, yet their properties are totally distinct; while the proteine theory professes to explain difference of properties by difference of composition. Thirdly: recent analyses, according to the most accurate methods, have proved that these bodies contain three or four times as much sulphur as is assumed in Mulder's formulæ. Fourthly: it has been found impossible to obtain a proteine free from sulphur; for if the operation be continued as long as sulphur is found in the precipitate, the result is that at last no precipitate at all will be obtained. As long as acetic acid causes a precipitate, that precipitate contains sulphur. Fifthly: the presence of phosphorus in any other form than that of phosphates, in albuminous substances, has in no way been established, and seems in the highest degree doubtful. Lastly: the best analyses we have render it very questionable whether, in reference to the carbon, hydrogen, nitrogen, and oxygen, the albuminous bodies agree so closely as is supposed on the theory of Mulder.

Since, then, the existence of proteine has not been demonstrated, there appears no good reason for adopting the proteine theory; and we shall therefore describe the albuminous bodies without further reference to it.

1. *Vegetable Albumen* has only been studied as yet in the

coagulated or insoluble state. It occurs, however, dissolved, or in the soluble form, in vegetables, and especially in the oily seeds, along with caseine. It is always combined with alkali, to which it owes its solubility. Its distinguishing character is that of coagulating or becoming insoluble when heated to from 140° to 160°. Once coagulated it no longer dissolves, even in the liquid in which it was formerly quite dissolved. When a fresh vegetable juice is filtered and boiled, it yields a coagulum, which is nearly pure albumen. Its solutions are also coagulated by acids, by infusion of galls, by creosote, and by corrosive sublimate. When dried, it is translucent. In all these characters it agrees with animal albumen. Its composition, so far as it has been ascertained, is the same as that of animal albumen; but the true formula, even of the latter, is unknown. We shall therefore state, under *Animal Albumen*, what is the result of the best analyses.

2. *Vegetable Fibrine* is the essential part of what is called the *gluten* of wheat. It is chiefly found in the seeds of the cerealia. When wheat, softened in water, is kneaded under water in linen bags to obtain the starch, and the residuary masses are beat up with rods, the pure fibrine adheres in elastic, transparent filaments to the rods. These, after being treated by ether, to remove fat oil, are pure fibrine. When dried, it becomes greyish and translucent, like horn. When heated, it yields the usual products of animal matters; and when left to itself in the moist state, it putrefies, disengaging fetid gases. It is quite insoluble in water. Diluted phosphoric and acetic acids dissolve it easily: these solutions are precipitated by ferrocyanide of potassium, and by infusion of galls. Diluted potash also dissolves it; and this solution, when neutralised by phosphoric or acetic acid, yields a precipitate which dissolves in an excess of either of these acids. For the composition of fibrine, see *Animal Fibrine*.

3. *Vegetable Caseine*, Syn. *Legumine*, is an essential part of the seeds of the leguminosæ, and also of the oily seeds. It is only known in combination with acids and with alkalies. To obtain it, kidney-beans, lentils, or pease, are softened in water, then brayed in a mortar, the pulp mixed with much cold water, and strained through a fine sieve, which retains the husks, and allows the caseine and starch to pass, the former dissolved, the latter suspended. On standing, the starch settles to the bottom, leaving a solution of caseine, which may be decanted. It is sometimes milky if much oil be present, sometimes clear. When exposed to the air, it quickly becomes acid, lactic acid being formed, and coagulates exactly as skimmed milk does when

it becomes sour. The solution of caseine does not coagulate by heat, but, like milk, forms a pellicle which is renewed as fast as it is removed. It is coagulated by the addition of an acid, and the coagulum dissolves in an excess of all vegetable acids, except acetic acid, which produces a permanent precipitate, as do the mineral acids. This precipitate is well washed with cold water, alcohol, and ether, dissolved in hot water with a little ammonia, and this solution is precipitated by alcohol. It still contains ammonia, but is otherwise nearly pure.

In this state it is like paste of starch, and when dried it is nearly transparent, and liquefies when heated. In water it softens, and this paste is coagulated by acids, corrosive sublimate, infusion of galls, and creosote. Caseine is very soluble in tartaric and oxalic acids, also in caustic and carbonated alkalies if diluted. The coagula, or precipitates formed by mineral acids in solutions of caseine, are compounds of caseine with the acid: they are soluble in strong acids. For the composition of caseine, the reader is referred to *Animal Caseine*.

4. *Emulsine*, or *Synaptase*, is the name given to a peculiar compound of this class, found in certain oily seeds, as in almonds, &c. An emulsion of these seeds is very like milk. On standing, the oil rises, like cream, to the top, and the watery liquid is now coagulated by acetic acid, as milk would be. It coagulates also by boiling; and in this case, the whey, separated from the coagulum, again coagulates on standing twenty-four hours, and is found to contain lactic acid. The emulsine agrees with albumen, in being coagulated by heat, and with caseine in being coagulated by acetic acid. It exerts a peculiar decomposing agency on amygdaline, in which it is also itself decomposed.

Fungine is the substance of which mushrooms are chiefly composed. Its true nature is uncertain, but it contains nitrogen.

Gliadine is the name given to the viscid ingredient of gluten. It contains sulphur, and approaches in composition to vegetable albumen. It is probably a mixture.

When a vegetable juice, containing one or more of these compounds along with sugar, is exposed to the air, oxygen is absorbed, and a change is commenced in the albumen, fibrine, caseine, gluten, &c., which is soon communicated to the sugar, causing it to undergo the vinous fermentation. The temperature rises, and occasionally the viscous fermentation takes place, producing lactic acid, gum, and mannite. During fermentation, a grey deposit is formed; this is yeast or ferment. When the whole of the azotised principles have not been decomposed or rendered insoluble, the liquid, if excluded from air, remains without further change: but if air be admitted, the alcohol is converted into acetic acid, oxygen being absorbed by the azotised matters, the contact of which causes the alcohol also to absorb oxygen. When the sugar is in excess, only part of it is converted into alcohol, and part of the azotised matter takes the form of insoluble yeast, the rest being decomposed. The saccharine and spirituous liquid undergoes no further alteration. All the above statements apply to the juice of the grape and to the formation of wines and vinegar.

When the juice, as that of the grape, contains tartaric acid, ethers are formed, which give the liquid a peculiar smell and flavour, such as œnanthic ether, which is characteristic of all wines. When a juice contains sugar and caseine, it is most apt to undergo the viscous fermentation, or, at least, the caseine favours the production of lactic acid from the sugar. But at a high temperature, such as 100°, butyric acid is formed, instead of lactic acid.

Vegetable fibrine, as it is found in wheat flour, is subject to continual alteration by contact with water; and in this state it has the singular property of converting starch into dextrine, a soluble gum, and then into sugar. This remarkable power is best seen in germinating grain, as in malt, of which a small part mixed with a large quantity of starch in a thick paste, and warmed to 150° or 160°, very soon renders the whole quite fluid and dissolved, and finally converts it into grape sugar. That part of the fibrine which acts on the starch has become soluble in water. It is called *diastase.*

Diastase is made by rubbing up malt with a little water, expressing the mixture, adding just enough alcohol to separate the albumen, and to allow the liquid to filter. The filtered liquid, mixed with more alcohol, deposits the diastase. It is purified by being repeatedly dissolved in water and precipitated by alcohol. It is finally dried at a temperature of 100° or 110°. Thus prepared, diastase cannot be a pure compound, but it possesses in a high degree the power of promoting the solution of starch, that is, its conversion into dextrine and sugar. One part of diastase can convert into dextrine, with a little sugar, no less than 2000 parts of starch. Diastase is evidently fibrine altered, and still more prone to change. Its solution cannot be kept, it becomes acid, and loses its action on starch.

Malt is made by softening barley in water, and then exposing it to the air in moderately thick layers, at a moderate temperature, turning it frequently. In about four days the seeds germinate, if they have not been allowed to become too hot, and if the air has had free access. As soon as the germ has acquired the length of the seed, the operation is checked by drying the seeds in a current of warm air. They now constitute malt. In this operation, much carbonic acid is given off, oxygen being no doubt absorbed; the azotised matter in the seeds has undergone a change, and has acquired the properties of diastase; and the starch has in part disappeared, its place being supplied by grape sugar and dextrine.

When the malt is infused in warm water, the metamorphosis of the starch is completed, and the whole dextrine passes into sugar, which dissolves, along with extractive matter and salts. The solution is called *must*. When sufficiently concentrated, hops and yeast are added, and fermentation being carried on, the result is *beer* or *ale*, according to the strength of the must. When the malt has been in part roasted, the beer becomes very dark-coloured, as in the case of *porter*.

To obtain grain spirit, the meal, either of barley, oats, or rye, or a mixture, is digested in warm water along with 1 part of malt for 4 of meal, till the mass, at first thick, becomes fluid, a proof that all the starch has been metamorphosed. Yeast is then added, and, after fermentation, the must or *wort* as it is called, is distilled and rectified. Potato spirit is obtained in the same way, only using potato starch, instead of barley meal or rye flour.

Many other vegetable matters, and many fruits, may be made to yield spirit, malt or diastase being used in all cases where starch is to be converted into sugar.

Potato spirit is accompanied by the hydrated oxide of amyle, or oil of potato spirit: grain spirit by an oily matter, consisting chiefly of margaric and œnanthic acids, probably in part as margaric and œnanthic ether, and of a volatile oil, called by Mulder *oleum siticum*, that is, oil of grain. Wine spirit, that is, *brandy*, contains œnanthic ether, and the spirit of molasses, or *rum*, owes its flavour to butyric ether. The oils which contaminate potato and grain spirit are offensive and even injurious to health: they are included by the Germans under the general term *Fuseloel*.

Panification. Bread may be made from any flour containing, as all good flour does, vegetable fibrine, sugar, and starch. The flour being made into a paste with warm water, and yeast being added, it is set aside in a warm place. After a time, more flour is kneaded into the mass, which has begun to rise, and the whole is now heated in the oven, or baked. The yeast induces the vinous fermentation in the sugar of the flour, and the alcohol and carbonic acid escaping, raise the bread and render it porous. The starch in general is little changed, but the sugar disappears, as well as a part of the gluten or fibrine. To avoid this loss, bread is now raised by means of carbonate of soda or ammonia and a diluted acid, which are added to the dough, and the effect is perfectly satisfactory. Equally good or better bread is obtained, and the quantity of flour which will yield 1500 loaves by fermentation, furnishes 1600 by the new method, the sugar and fibrine being saved. The addition of a little alum to the dough is useful in arresting that decomposition in the flour which is apt to occur if it have been kept in a moist place. Too much alum cannot be introduced, as it would prevent the fermentation.

The nutritive properties (using the word in its strict sense) of different kinds of flour or meal are directly proportional to the fibrine or albumen they contain ; because it is these substances alone which can be converted into blood or flesh. Hence a working man requires more oat bread than wheat bread to restore the daily waste of the body, oatmeal containing rather less fibrine, &c. than wheat flour. The starch is consumed in the body, up to a certain point, but beyond this it is discharged in the excrements. We shall see hereafter what its function probably is. Even the best wheat flour contains more starch than is consumed ; and the excess is greater in other grains.

In germination, the azotised principles of the seeds become soluble and prone to further change. When now dissolved, they are in the same state as those of the grape juice which at once cause fermentation when air is admitted. Diastase is merely gluten, that is, fibrine, in this soluble form or period of change.

When left in water, gluten swells, putrefies, and disengages carbonic acid, hydrogen, and sulphuretted hydrogen gases : it then becomes fluid and ropy, the water becomes very acid, and contains a peculiar compound called caseous oxide, with acetate, phosphate, and caseate of ammonia. When vegetable caseine putrefies, it gives out the odour of putrid cheese, and yields sulphuretted hydrogen gas.

Ferment, Yeast, Lees of Wine. These are names given to the deposit formed in fermenting liquids, which possess the property of exciting fermentation in must, wort, grape juice, infusion of malt, or solution of sugar. When solution of sugar is employed in excess, the ferment gradually diminishes, till about

15 per cent. are left, of a substance containing no nitrogen, and insoluble. This is *cellulose*, or *hordeine*. On the other hand, in grape juice, or infusion of malt, the ferment is reproduced from the azotised principles present.

Mulder and Schlossberger have shown that ferment is composed of regular cells, formed of cellulose, and containing an azotised matter, very easily decomposed, which is an albuminous compound. This body rapidly decomposes the deutoxide and persulphuret of hydrogen, but loses this property after it has been heated to 212°. Mulder thinks that, after boiling, it is a superoxide of proteine.

The power of yeast or ferment to act on sugar is destroyed by boiling water, by absolute alcohol, by pyroligneous acid, salts of mercury, essential oils, sulphurous acid, &c.

Caseous Oxide, *Caseic Acid*, or *Aposepidine*, are names given to the crystalline compound formed during the putrefaction of gluten under water. It contains nitrogen, but its formula is unknown. It is soluble in water, insoluble in alcohol.

We now proceed to the consideration of the parallel compounds, *animal albumen*, *fibrine*, and *caseine*.

5. *Animal Albumen* is hardly known in a state of purity. The purest appears to be that prepared by exactly neutralising serum of blood or white of egg with acetic acid, and adding a large quantity of water. The albumen separates in translucent flocculent masses, which, when washed with water, assume the aspect of paste. (Denis.) Albumen is best known in the form of the serum of the blood and that of white of egg.

Serum of blood, dried in a very gentle heat, leaves a translucent mass, which dissolves completely by digestion with water. Both in this form, and in the preceding, it dissolves far more easily in the most diluted alkaline solutions.

White of egg consists of very delicate cells, filled with a ropy liquid. By beating with water, the cells are broken, and are afterwards deposited, being insoluble. Dried at a gentle heat, white of egg is yellow, translucent, and brittle. In water it again softens into its original state. When calcined, it leaves 6 or 7 per cent. of salts, common salt, carbonate, phosphate, and sulphate of soda, and phosphate of lime.

The action of heat on albumen is remarkable. When heated alone, or after dilution with water, to between 145° and 165°, it coagulates into the well-known white elastic mass, which, when dried, becomes yellow, horny, and brittle. It is now quite insoluble in water; but if, after being coagulated and dried, it is placed in water, it swells up into the original elastic mass of coagulated albumen.

The albumen prepared by the process of Denis dissolves readily not only in acids and alkalies, but also in neutral salts, such as nitrate or sulphate of potash or soda. It is owing to the presence of such salts in serum and white of egg that their albumen is soluble in water. When the pure albumen of Denis is dissolved in solution of nitre, it is coagulated by boiling, exactly like serum.

Solutions of albumen are coagulated by acids; the addition of free alkalies prevents even the action of heat. Serum and white of egg, when mixed with water, being both alkaline, may be neutralised carefully by acids, without coagulation. Acid solutions of albumen are precipitated by corrosive sublimate and ferrocyanide of potassium, by infusion of galls, by creosote, and by alcohol. The real difference between soluble and insoluble or coagulated albumen is not yet known.

When albumen putrefies, it yields sulphuret of ammonium, sulphuretted hydrogen, and other products. When heated, it burns with the odour of burnt horn or animal matter.

The composition of albumen is not yet ascertained with sufficient precision to enable us to deduce its formula from the analysis alone. The following table contains a few of the best analyses of the albumen of eggs:—

	Mulder.	Scheerer.	Rüling.	Verdeil.	
Carbon	54·086	55·000	51·91		
Hydrogen	7·100	7·073	7·15		
Nitrogen	15·650	15·920			
Oxygen	22·157	22·007			
Phosphorus	00·330				
Sulphur	00·667		1·717	2·164	2·054

A glance at these numbers is sufficient to show that the agreement is not such as to enable us to fix a formula, and more especially such a formula as that of Mulder, containing 10 eq. of proteine, that is, 400 eqs. of carbon, 310 of hydrogen, 50 of nitrogen, and 120 of oxygen. A very trifling variation in the carbon, for example, makes a difference of 20, 30, or more atoms in the deduced formula, and the above analyses exhibit a variation of 3 per cent. in the carbon. Again, the sulphur in the analyses of Rüling and Verdeil amounts to more than 3 times the quantity obtained by Mulder, who admits 1 eq. of sulphur in egg-albumen. The presence of phosphorus, as admitted by Mulder, has not been proved; and lastly, the most recent analyses indicate from 16 to 17 per cent. of nitrogen.

It is clear, therefore, that we cannot hope to fix the formula of albumen by mere analysis, at least for the present; and the only method which promises better results, is the study of the products of its decomposition. In the case of gelatine and caseine, a beginning, as we shall see, has been made, and it is more than probable that albumen will yield similar results.

6. *Animal Fibrine* is found in blood, chyle, and lymph dissolved, and forms the chief part of the muscles. It may be obtained by whipping up blood with rods, when it adheres to the rods, and is finally purified by kneading with water to remove colouring matter, and by digestion with alcohol and ether, which dissolve fatty substances. When dry it is somewhat similar to albumen, and when heated burns with the same smell, leaving from 0·77 to 2·55 per cent. of ashes, phosphates of lime and magnesia. Recent fibrine loses, in vacuo, about 80 per cent. of water, the greater part of which it again takes up when placed in water. When long boiled with water, it slowly dissolves; and when left long, that is, for some months, under water, it gradually disappears.

The fibrine of venous blood dissolves, at a gentle heat, in solutions of acetate of soda, sal-ammoniac, and nitre. These solutions are coagulated by heat, and exhibit the properties of dissolved albumen. Muscular fibrine may also be thus dissolved; but neither arterial fibrine, nor the fibrine of the buffy coat, can undergo this change. Venous fibrine loses this property by exposure to the air, when it absorbs oxygen and gives off carbonic acid. Fresh fibrine rapidly decomposes deutoxide of hydrogen: but boiling water or alcohol deprive it of this property.

The most striking character of fibrine is its spontaneous coagulation, as in the blood; which is also seen in vegetable fibrine in some juices. In regard to acids and alkalies, fibrine acts like albumen.

The composition of fibrine approaches closely to that of albumen, and the best analyses do not admit of being reduced to a formula at present. We may hope for a better result when the products of its decomposition shall have been minutely studied.

7. *Animal Caseine* is chiefly found in *milk*. It is not known in a state of purity, but only combined with bases or acids, for both of which it has a powerful attraction. Uncombined caseine is insoluble: in milk it is dissolved by virtue of the potash which renders that fluid alkaline. If carefully neutralised by an acid, milk is not coagulated, but it is then coagulated by boiling. The coagulum or curd formed by excess of acids is

very soluble in oxalic and tartaric acids, sparingly so in the mineral acids. This coagulum contains, along with caseine, a good deal of the acid employed.

The coagulum caused in milk by alcohol yields, when burned, 10 per cent. of ashes, chiefly phosphate of lime. What is called soluble caseine is a compound containing much potash. With lime, baryta, &c., caseine forms insoluble compounds.

The composition of caseine is not accurately known, as the body known under that name contains 6·5 per cent. of ashes. But in regard to the other elements it agrees pretty nearly with albumen and fibrine, the existing analyses exhibiting the same variations. It certainly contains less sulphur than albumen or fibrine, for while albumen contains from 1·7 to 2 per cent., and fibrine from 1·3 to 1·6 per cent., caseine appears to contain no more than from 0·85 to 1·0 per cent. of sulphur.

As in the case of the two preceding compounds, so also in this, no formula can safely be deduced from the analyses. But the study of the products of decomposition of caseine, which has been commenced, promises to lead to better results.

Schlossberger has succeeded in resolving caseine into two nitrogenised bodies, one of which contains all the sulphur, the other none. Liebig has discovered that when caseine is melted with caustic potash till hydrogen gas begins to escape along with ammonia, the residue, dissolved in water, and mixed with acetic acid, deposits a crystalline compound *tyrosine*, $C_{16}NH_9O_5$, which merits a detailed investigation. The mother liquid, when further concentrated, yields *leucine*, a body already known as a product of the action of potash on gelatine. Its formula is $C_{12}NH_{12}O_4$.

Moreover, if the original fused mass be supersaturated with tartaric acid, and distilled, it yields valerianic acid; and if the heat has been longer continued, butyric acid also is obtained. The origin of the valerianic acid is obviously the action of potash on leucine previously formed.

$$\underbrace{C_{12}NH_{12}O_4}_{\text{Leucine.}} + 3(KO, HO) = \underbrace{KO, C_{10}H_9O_3}_{\text{Valerianate of Potash.}} + NH_3 + 2(KO, CO_2) + H_2.$$

Leucine contains, excepting 1 eq. of hydrogen which is wanting, the elements of a compound of 1 eq. cyanic acid, 1 eq. oxide of amyle, and 2 eqs. of water.

$$C_{12}NH_{12}O_4 + H = C_2NO + C_{10}H_{11}O + 2HO.$$

But when hydrated cyanic acid is made to act on hydrated oxide of amyle, it yields a compound which, although very similar to leucine, is yet quite distinct, being the allophanate of oxide of amyle, analogous to the allophanate of oxide of ethyle. Its formula is

$$C_{14}N_2H_{14}O_6 = \underbrace{C_{10}H_{11}O}_{\text{Oxide of Amyle.}} + \underbrace{C_4N_2H_3O_5}_{\text{Allophanic Acid.}}$$

According to Bopp, caseine, when acted on by hydrochloric acid, yields products, among which are found, in large proportion, tyrosine and leucine. It has long been known that albuminous bodies yield leucine when acted on by sulphuric acid. It appears, therefore, that these compounds have a tendency to yield definite and crystalline products, the study of which offers the best method of ascertaining their formulæ.

It has also been found that caseine, when oxidised by certain methods, yields the same varied products as gelatine. (See gelatine.)

In the spontaneous decomposition of caseine we again meet with valerianic acid, along with butyric acid and the other volatile oily acids.

Milk, or any other solution of caseine, when evaporated in the air, forms a pellicle, which is renewed as fast as it is removed. This is insoluble, and yields ashes containing lime and phosphate of lime.

Milk may be analysed by drying it up in vacuo, dissolving the butter by a mixture of ether and alcohol, and the sugar of milk and salts by cold water. The caseine remains in this way undissolved, the salts having been first removed.

When exposed to the air, milk undergoes a peculiar change. The caseine enters into decomposition, and this decomposition passes to the sugar of milk, which yields a little lactic acid, and this causes the caseine not yet decomposed to coagulate. But the decomposition continues: the sugar of milk is at last entirely converted into lactic acid, mannite and gum; and if the acid be neutralised, and fresh sugar added, it will undergo the same change as long as any caseine remains. This is the method followed for obtaining lactic and lactates. The coagulum, separated from the whey when first formed, and pressed out, forms cheese. In making the better kinds of cheese, the milk, instead of being allowed to coagulate spontaneously, is coagulated by contact with water in which part of the lining membrane of a stomach has been infused. This infusion is called rennet, and it acts by virtue of containing albumen or gelatine in a state of decomposition, which is at once communicated to the sugar.

When milk, spontaneously coagulated, is exposed to a heat of from 75° to 85°, without any addition, the sugar of milk passes into grape sugar, and vinous fermentation ensues. The fermented milk, distilled, yields a spirit containing traces of butyric ether.

If sugar is made to ferment with caseine at about 100°, carbonic acid and hydrogen gases are disengaged, and butyric acid is formed in large quantity.

The chief mineral substances in milk are potash and phosphate of lime, which are found in its ashes. The ashes also contain sulphates, although milk does not. The sulphuric acid in the ashes is derived from the oxidation of the sulphur of the caseine.

The proportions of water, caseine, sugar of milk, butter, and salts, are very variable in milk. It generally contains about 86 per cent. of water, 4 to 7 of caseine, 3·5 to 5·5 of butter, and 3 to 5·5 of sugar of milk and salts. For the best method of analysing milk, proposed by Haidlen, I must refer to the "Annalen der Chemie und Pharmacie, xlv., 274." By this method Haidlen obtained as follows:—

	From Cow's Milk.	Human Milk.	Do.
Butter	3	3·4	1·3
Sugar of Milk, and salts soluble in alcohol	4·6	4·3	3·2
Caseine and insoluble salts . . .	5·1	3·1	2·7
Water	87·3	89·2	92·8
	100·0	100·0	100·0

The colostrum, or milk given immediately after parturition, differs from normal milk in containing 15 to 25 per cent. of albumen, with less caseine, butter, and sugar of milk.

The milk of bitches, according to Simon, contains from 14·6 to 17·4 of caseine, 16·2 to 13·3 of butter, and no sugar.

Cheese is caseine in a state of incipient or progressive decomposition or putrefaction. In the finer kinds of cheese, there is a large proportion of butter, and to the volatile acids of the butter may be ascribed the flavour of cheese. Some kinds of cheese are full of what are called eyes, that is, hollows, caused by the formation of bubbles of gas; and in these hollows a liquid is sometimes found, containing free ammonia, a product of decomposition, which greatly heightens the flavour. When the blue mould appears in cheese, it is in a state of rapid decay or eremacausis, and much ammonia is given off. Little is yet known of the chemical differences in the making of different kinds of cheese. The richest are made almost entirely from cream, as Stilton and Parmesan. Others, as Gruyère, Gloucester, Cheshire, and Dutch cheese, are made with fresh uncreamed milk, or mixtures of this with cream; and more or less salt is used, as well as different methods of coagulating, in different places.

Animal Mucus is somewhat analogous to albumen, when dry. In water, it softens and swells, like tragacanth. It is precipitated by picric acid. It contains sulphur.

8. *Horny Matter.* This name may be given to the substance of which the epidermis, hair, wool, silk, feathers, nails, claws, hoofs, horn, shell, and probably also sponge, are composed. All these substances dissolve in potash-ley when heated with it, giving off ammonia, and forming a solution from which, by neutralisation with acetic acid, a white gelatinous matter is precipitated. (See *Proteine*). They all contain sulphur. Sponge leaves 3½ per cent. of ashes, among which is found iodide of potassium. All the above substances, when heated or burned, give out the same peculiar and well-known smell, known as that of burnt feathers.

GELATIGENOUS TISSUES.

Under this head we place several tissues which yield to boiling water a substance which on cooling forms a jelly, or may be called *gelatine.* They are chiefly found in the cellular membrane, the skin, the membranes in general, the tendons, ligaments, bones, cartilages, &c.

The cellular tissue and the membranes are chiefly formed of gelatinous matter, which is insoluble in cold water and acids. It combines with salts, as corrosive sublimate, persulphate of iron and alum, forming insoluble compounds which do not putrefy, as gelatine itself so readily does.

The gelatine of the skin, when moist, combines with tannic acid, if steeped in a solution of that acid, and is converted into leather. While the true skin is gelatinous, the epidermis is more allied to horn.

Chondrine is the name given to the gelatine of the cartilages.

Gelatine or *Glue* is that given to the gelatine of the bones and hoofs, skins, &c. of animals. Isinglass is made from the air-bladder of fishes, and is nearly pure gelatine.

1 part of pure gelatine, dissolved in 100 of hot water, forms a jelly on cooling. A solution of isinglass is completely precipitated by infusion of nut galls.

Chondrine and gelatine, in solution, are distinguished by acids, alum, and salts of lead, which precipitate chondrine but not gelatine. In regard to other tests, they agree. $\frac{1}{5000}$ of either may be detected by tannic acid.

By the action of chlorine on gelatine, there is formed what is called *chlorite of gelatine*, consisting, according to Mulder, of chlorous acid and gelatine.

By the action of potash, gelatine is converted into sugar of gelatine, or glycocoll, a substance already described as an artificial base, or into a mixture of sugar of gelatine and leucine.

The composition of gelatine is not more accurately known than that of the albuminous substances already mentioned. It approaches to them in composition, but, so far as we know, it cannot pass into albumen, fibrine, or caseine, as these bodies can pass into each other, and even into gelatine. Hence it is not fitted for the formation of blood, and cannot be called strictly nutritious.

When gelatine is oxidised by means of bichromate of potash and sulphuric acid, it yields, according to Schlieper, the following products: 1, hydrocyanic acid; 2, acetic acid; 3, valerianic acid; 4, benzoic acid; 5, a new oil, *valeronitrile;* 6, another new oil, *valeracetonitrile;* and, 7, a heavy oil, with an odour of cinnamon, not fully studied. Marchand obtained also hyduret of benzoyle.

Valeronitrile, $C_{10}H_9N$, corresponds to *benzonitrile*, a compound recently discovered among the products of the action of heat on benzoate of ammonia; and may be derived from valerianate of ammonia, as follows:

$$\underbrace{C_{10}H_9O_3,\ NH_3,\ HO}_{\text{Valerianate of ammonia.}} = 4\,HO + \underbrace{C_{10}H_9N}_{\text{Valeronitrile.}}$$

When acted on by alkalies, it takes up water, and is again converted into valerianic acid and ammonia.

Valeracetonitrile, $C_{26}H_{24}N_2O_6$, contains the elements in 2 eqs. of 4 eq. valeronitrile, and 3 eqs. hydrated acetic acid. It is resolved by alkalies, water being taken up, into ammonia, which escapes, and acetic and valerianic acids.

It is obvious that the full investigation of the products of decomposition of gelatine will ultimately lead us to its true formula.

Bone. The gelatine and other animal matters in healthy bone constitute from 37·5 to 44 per cent.; the rest is earthy matter. In rickets and mollities ossium, the cartilaginous matter amounts to from 63 or 70 to 80 per cent., and the phosphate of lime is diminished in proportion, not exceeding, in some cases, 12 or 13 per cent.

The proportions of gelatine and earthy matter vary in different animal species.

The earthy ingredients of bone are, phosphate of lime, carbonate of lime, fluoride of calcium, phosphate of magnesia, with small quantities of common salt, soda, &c.

Bone or *Ivory Black*, obtained by calcining bones in retorts, contains all the earthy and saline matters, with a large proportion of charcoal intimately mixed with them. It probably contains nitrogen. Qu ? as paracyanogen or mellone ?

THE BILE.

This animal fluid, collected from the liver in the gall-bladder, is slightly alkaline, and has a viscid, oily consistence. It has, when fresh, a golden-yellow colour with a tinge of green, and becomes darker when exposed to the air. Its taste is bitter and persistent, with a sweetish after-taste. It is perfectly miscible with water, and its aqueous solution froths like solution of soap.

When dried in the vapour-bath, bile leaves a yellow mass, which dissolves in alcohol, leaving undissolved a little mucus. The alcoholic solution is deep green, but may be decolorised either by animal charcoal, or by the cautious addition of baryta, which forms an insoluble compound with the colouring matter. The decolorised alcoholic solution of bile still contains cholesterine, which is separated by adding ether, till the solution becomes slightly turbid ; on standing, pure bile is deposited in crystals, the formula of which is $NaO + C_{44} H_{40} NSO_9$. (Verdeil.)

The solution of bile is precipitated by neutral acetate of lead, but the liquid becomes acid. If the free acid be neutralised, acetate of lead produces a fresh precipitate, the liquid again becoming acid. Tribasic subacetate of lead precipitates at once the whole of the organic matter of the bile, but an excess of the precipitant is apt to redissolve a part of the precipitate, which is also soluble in alcohol. Mineral acids cause a resinoid precipitate in solution of bile.

Bile in solution may be recognised by the property of striking a purple colour with solution of sugar and sulphuric acid.

Purified bile, when calcined, leaves a white ash, composed chiefly of carbonate of soda, with traces of phosphate of soda and common salt. The ash amounts to 12 per cent., of which upwards of 11 consist of carbonate of soda.

It is, therefore, evident that bile is composed of soda united to an organic compound, having the characters of an acid, although a feeble one, and in some respects analogous to the fatty and resinous acids. This compound, which is the whole organic or combustible part of the bile, is called *choleic or bilic acid*, and bile is the *choleate of soda.*

Choleic acid is best prepared by making an alcoholic solution of 8 parts of pure bile, and dissolving, with the aid of heat, in this, 1 part of effloresced (monohydrated) oxalic acid. The oxalate of soda separates in crystals. The filtered liquid, diluted with a little water, is digested with carbonate of lead, till all oxalic acid is removed. Any lead that may be dissolved is separated by sulphuretted hydrogen, and the filtered solution evaporated in the water heat. Choleic acid may also be obtained by the action of dry hydrochloric acid gas on a solution of pure bile in absolute alcohol, and by several other processes, of which one may be noticed. Pure bile is precipitated by subacetate of lead, and the precipitate brought with water to the boiling point. Sulphuric acid is now added, drop by drop, until the precipitate has lost its peculiar consistence. The liquid is then filtered, and any dissolved lead separated by sulphuretted hydrogen.

To purify choleic acid it is dissolved in a very small quantity of alcohol, and precipitated by ether, which retains in solution fatty matters. The probable formula of choleic acid is $C_{44}H_{40}NSO_9, HO = C_{44}H_{41}NSO_{10}$.

When dried in the water-bath, or in vacuo, over sulphuric acid, choleic acid, if prepared from decolorised bile, is colourless, or nearly so, and has the aspect of gum. It is resinous and friable when dry, but its powder attracts moisture strongly, and becomes agglomerated together. Its solution is distinctly acid to test-paper. The addition of mineral acids causes a separation of choleic acid in oily drops, which are soluble in pure water.

Pure choleic acid, when heated on platinum foil, burns with flame, leaving a voluminous coal which finally burns away without residue of ashes. When choleic acid leaves an alkaline ash, it is because it contains undecomposed bile, choleate of soda; in fact, it may be called acid choleate of soda, a substance which has been described as a distinct ingredient of the bile by several chemists.

Numerous analyses of pure bile (deducting the ashes) and of choleic acid, both prepared in many different ways, by different chemists, as Demarçay, Theyer and Schlosser, Kemp, Enderlin, Verdeil, and others, agree so well together, that no doubt can be entertained in regard to this point, that the bilic or choleic acid of ox bile is a substance of uniform composition, and that the acid in bile has the same composition as that which is obtained in the separate state by the processes above given.

Further, if the choleate of lead, purified from phosphate, chloride, &c., of lead by solution in alcohol, be acted on by carbonate of soda, choleate of soda (artificial) is obtained; and this salt, when pure, is found to differ in no one respect from pure bile, or natural choleate of soda, and is, therefore, regenerated bile. Its composition is the same as that of bile.

Choleate of soda has already been described as purified bile.

Acid choleate of soda has been at different times known as *biliary matter*, and as *bilifellic acid with excess of biline* (Berzelius). But the biline of this chemist, and also his sugar of bile, are nothing more nor less than either pure bile or choleic acid. Platner has lately obtained the acid choleate of soda crystallised, which is a strong additional argument in favour of the opinion that the bile is a uniform and definite compound of choleic acid, and that all the numerous compounds described by Berzelius and others as constituents of bile, are products of the decomposition of choleic acid. This is a consideration of the utmost importance, with reference to the production of bile in the animal body, to its functions, and in short to chemical physiology.

Choleate of lead (basic). This salt, precipitated by subacetate of lead, has the characters of a plaster, as choleate of soda has those of a soap.

PRODUCTS OF THE DECOMPOSITION OF BILE.

The recent discovery of 38·6 per cent. of sulphur in taurine, and of nearly 4 per cent. in choleic acid, renders it impossible to give at present a satisfactory account of the various metamorphoses of the bile until the researches, rendered necessary by these discoveries, shall be concluded. In the meantime, the only compounds the formulæ of which are known with any degree of certainty, are choleic acid and taurine. The formula of cholic acid must be considered doubtful, till we know what becomes of the sulphur of the bile in its formation.

1. *Choloidic acid.* This acid is formed by the action of hydrochloric acid, when boiled with bile. It differs from choleic acid in containing no nitrogen. Its formula is $C_{60}H_{50}O_{11}$. Its production is attended with the formation of *taurine*. Choloidic acid is resinous or rather pitchy in aspect, softened by the heat of boiling water, insoluble in water and ether, soluble in

alcohol. Probable formula $C_{60} H_{50} O_{11} = C_{60} H_{49} O_{10}, HO$; but as that formula was ascertained before the presence of sulphur in choleic acid was known, it must be considered doubtful.

By the action of nitric acid, choloidic acid is converted into a variety of products, among which are—1. Several of the oily acids of the series $(CH) n + O_4$. 2. A heavy pungent volatile oil, which by the action of potash yields *nitrocholic acid*, $C_2 H N_4 O_9, HO$, and *cholacrole*, another pungent oil, $C_8 H_5 N_2 O_{13}$; 3. *Choloidanic acid*, $C_{16} H_{11} O_6, HO$, and 4. *Cholesteric acid*, $C_8 H_4 O_4, HO$, so called because it is also formed by the action of nitric acid on cholesterine.

2. *Taurine*, $C_4 H_7 NS_2 O_6$. This substance is found in the liquid which has deposited the choloidic acid. When pure, it forms large prisms, neutral, with a cooling taste, soluble in water, and very permanent, not being decomposed by strong nitric acid.

3. *Cholic acid*. This is another non-azotised acid, formed when bile is acted on by fusion with caustic alkalies, which disengage the nitrogen as ammonia. It resembles the fatty acids, or rather the resinous acids. It forms large transparent tetrahedra, soluble in alcohol and ether, nearly insoluble in water. Formula, $C_{42} H_{32} O_8, HO$?

4. *Dyslysine*. This is the name given by Berzelius to a compound formed during the action of hydrochloric acid on bile. It is very sparingly soluble in hot alcohol. (Hence its name, from δυς, difficult, and λυσις, solution). It has a resinous aspect, and the formula $C_{60} H_{46} O_7$, that is, choloidic acid *minus* 4 eq. water.

The *fellic acid* and *cholinic acid* of Berzelius are mixtures of some of the above, or of other products, with unaltered choleic acid. They do not exist ready-formed in bile, according to Theyer and Schlosser.

5. *Cholic acid* (Gmelin). This is an acid, containing nitrogen, formed when choleate of lead is acted on by acetic acid. It forms fine needles of a sweet and pungent taste, very soluble in alcohol and in hot water. Its formula is unknown.

6. *Cholanic acid* is a resinoid acid, found in putrid bile, and very similar to choloidic acid, if not identical with it.

7. *Fellanic acid* accompanies the preceding. It forms transparent prisms, and may possibly be cholinic acid. At all events, it is not established as a distinct compound; but is a product, probably a mixed one, of some of the changes of so complex a substance as choleic acid.

The colouring matter of the bile when dry is reddish-brown, but dissolves in potash with a yellow colour, becoming greenish-brown in the air. Its solution, mixed with excess of nitric acid, becomes first green, then blue, violet, red, and finally yellow. The same changes of colour are seen in serum, chyle, or urine charged with bile, as in jaundice.

BILIARY CONCRETIONS.

The calculi or concretions found in the gall-bladder are generally composed of cholesterine, with more or less colouring matter. Sometimes the cholesterine is so pure that alcohol dissolves it entirely and becomes hardly coloured; at other times colouring matter alone is found. The former case occurs in the human subject: the latter generally in the ox.

Lithofellic acid is an acid found constituting the mass of certain concretions called *bezoar orientale*, and said to be found in the stomach of certain antelopes; but which are, no doubt, biliary concretions.

Lithofellic acid is fusible, gives off when heated a fragrant vapour, and has when cut or rubbed in the concretion the lustre of wax. It dissolves in hot alcohol, and forms brilliant six-sided prisms, insoluble in water. Formula, $C_{42} H_{38} O_8$ (Ettling and Will); $C_{40} H_{35} O_7$, HO (Wöhler).

Nitric acid converts it into a new acid containing nitrogen. Formula, $C_{40} H_{28} NO_{11}$.

When distilled, lithofellic acid loses 2 eq. water, and yields pyrolithofellic acid, $C_{40} H_{34} O_6$.

BRAIN AND NERVOUS MATTER.

This substance consists of water to the extent of about 80 per cent.; of albuminous matter, 7 per cent.; and of several peculiar fats, among which are cholesterine, and another beautifully crystalline fat, resembling cholesterine but distinct from it.

Cerebric acid. This is a fatty acid, peculiar to the nervous matter. It is purified by means of ether, which removes an oily matter, and by crystallisation in hot alcohol. It forms white granular crystals, slightly soluble in water, especially when hot, although the greater part is not dissolved but swells up into a gelatinous paste. It melts when heated, and when burned leaves a very acid coal. It contains both nitrogen and phosphorus, which distinguishes it from the ordinary fat acids. Its salts are very soluble in alcohol, as well as in water.

Oleophosphoric acid. This acid is dissolved, in combination with soda, by the ether used in purifying cerebric acid; but it is hardly known in a state of purity, being mixed with a neutral oil, *cerebroleine*, with cholesterine, and with cerebric acid, in small quantity. With alkalies it forms soaps, exactly similar to the salts dissolved from brain by ether. When boiled with water or alcohol, it is resolved into *cerebroleine* and phosphoric acid. Of the latter it yields about 2 per cent.

Cerebroleine is purified by cold alcohol, which dissolves the oil, leaving undissolved all the cholesterine and cerebric acid. Its composition is the same as that of the oleine of human fat.

The cholesterine of the brain appears to be identical with that of bile. The brain also contains traces of oleic and margaric acids. When it putrefies, the oleophosphoric acid disappears entirely.

The most important point in the chemical history of the brain is that it contains both fat and albumen, the two extremes of the animal products, and substances (cerebric and oleophosphoric acids) of a composition intermediate between that of albumen and that of fat. These bodies, however, appear to contain even a larger proportion of phosphorus than albumen. It is not yet known where the cerebric and oleophosphoric acids are produced : whether in or by a special organ, as the bile is by the liver ; or whether in the circulation generally. It will be seen hereafter that the blood does contain traces of cholesterine and other fatty matters ; and, indeed, as the blood also contains bile, it may be supposed that the liver does not form the bile but merely separates it from the blood, it having been previously formed. In like manner, even if there should be found an organ connected with the formation or secretion of nervous matter, still the function of that organ might be only to separate cerebric acid, previously formed, from the blood. At all events, we cannot doubt that the very remarkable composition of the acids of the brain has an important relation to the functions of that organ, and that the production of those acids forms an essential part of the vital process going on in the body.

Liebig has lately observed that the brain contains no kreatine (a body found in urine and in the juice of flesh), but that when triturated with barytic water, two acids are taken up by that base, forming salts, one of which is insoluble, the other soluble, in alcohol. Both dissolve in water, and the solution in both cases yields a white precipitate with acids. The acids in question are therefore insoluble in water, and probably allied to fat acids, but they have not yet been examined.

Dr. R. D. Thomson has also been for some time engaged in the study of the brain, and his researches are anxiously looked for.

GASTRIC JUICE.

This juice, as extracted from the stomach of executed criminals, is colourless or slightly yellow, turbid, and distinctly acid. It contains free acids along with chlorides of potassium and sodium.

The nature of the free acid present in the gastric juice has been disputed. When it is distilled, free hydrochloric acid is obtained, and this is often, perhaps always accompanied by butyric acid. But it must be remembered that these acids are volatile, and that therefore their presence in the distilled liquid affords no proof of their existence in the free state in the gastric juice. On the other hand, Lehmann obtained from the gastric juice, by a peculiar process, a salt of magnesia, which he analysed, and which Liebig has shown to be lactate of magnesia. There can be no doubt of the presence of phosphoric acid, free or combined; and it is most probable that in the normal juice, the fixed acids, phosphoric and lactic, are, in part at least, free, while the volatile acids, hydrochloric and butyric, are present in the form of salts. In the distillation, the latter are expelled in the free state, the fixed acids taking their place. This view is confirmed by the phenomena exhibited by the juice of flesh, (See Liebig's Researches on the Chemistry of Food, and the next section of this work,) which undoubtedly contains free lactic and phosphoric acids, (or what is the same thing, acid phosphates and acid lactates,) along with chlorides, and appears to have a very close resemblance to the gastric juice.

The property of dissolving or digesting food such as albumen, fibrine, caseine, &c., is owing in part to the presence of free acid, and in part to the presence of part of the lining membrane of the stomach dissolved, and in a state of change. The gastric juice converts into chyme, or digests, albumen, fibrine, &c., out of the body as well as in it, if the temperature of the stomach be kept up; and water acidulated with a trace of hydrochloric acid, and afterwards left for 24 hours in contact with the lining membrane of a stomach, acquires in a very high degree the solvent power of the gastric juice. Water thus prepared dissolves in 8 to 12 hours, at the temperature of from 86° to 104°, hard-boiled white of egg, &c., which requires 4 days at a temperature of 158° to 176° to be dissolved by water merely acidulated with the same proportion of acid, but not placed in contact with the stomach. This latter fluid, however, dissolves meat better than it does albumen, because the meat supplies some membranous matter in a state of change, by which the solution of the fibrine is finally promoted.

All attempts to isolate the supposed principle—*pepsine* as it was called, which is supposed by some to be the solvent of food in the stomach—have failed. The gastric juice has only yielded traces of animal matter, and we have not yet any proof that its solvent action depends on a peculiar compound, and is not rather the effect of a kind of fermentation induced in the food by contact with the particles of the dissolved epithelium, themselves in a state of change, and consequently of motion. On the whole, then, taking into account the facts of artificial digestion, it appears most probable that digestion is a process analogous to fermentation in the conditions under which it takes place, namely, a certain temperature, and contact with azotised matter in a state of decomposition ; but differing from the usual forms of fermentation in its phenomena, no gas being disengaged, and its chief result being the solution of an originally insoluble matter.

JUICE OF FLESH.

The muscular mass of animal bodies is chiefly composed of muscular fibre (fibrine), coloured by blood, contained in innumerable small vessels, of those vessels, of nerves, of tendinous matter, and of cellular tissue. More than $\frac{3}{4}$ths of its weight are water, which, holding in solution a great variety of substances, penetrates every part of the mass, and constitutes the *juice of flesh*, as it is termed. This fluid is contained either in peculiar minute vessels or in the cells of the cellular tissue, and when the flesh is finely chopped and pressed, the juice is obtained, more or less mixed with blood. The best method is to mix the chopped flesh with water, to squeeze out the mass, and to repeat this process if necessary. In this way, the juice of flesh is obtained in a somewhat diluted state, and, as already stated, not free from blood.

This fluid has recently been studied by Liebig (Researches on the Chemistry of Food *) with very interesting results. It is uniformly and strongly acid, and the acids present are lactic acid, in large quantity, phosphoric acid, a new azotised acid, *inosinic acid,* and in smaller quantity some other organic acids, not yet examined. No sulphuric acid is present, save a trace from the blood. The bases are potash in large proportion, both as phosphate, lactate, inosinate, &c., and as chloride of potassium ; soda in much smaller quantity, chiefly as chloride of sodium, (and probably derived from the blood, at least for the most part) ; magnesia ; lime ; the latter in much smaller proportion ; and kreatinine. The juice contains, besides, albumen dissolved, which is coagulated by heat, and amounts to from 2 to 3 per cent. of the weight of the flesh. The insoluble residue of fibrine, &c., amounts when dry to 17 or 18 per cent., so that the average composition of flesh will be nearly as follows :—

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* London : Taylor and Walton. 1847.

	Water	78
	Fibrine, vessels, nerves, cells, &c.	17
Soluble matter.	Albumen	2·5
	Acids and bases, organic and inorganic, chlorides, and Kreatine	2·5
		100·0

It is obvious that in order to study with success the soluble matters not coagulated by heat, we must operate on large quantities of flesh, since, for example, 10 lbs. of flesh will not yield more than 4 oz. of these substances, among which are five or six acids, and as many bases, besides chlorides and kreatine. Thus, from 10 lbs. of beef, only about 50 grains of kreatine can be obtained.

Kreatine. This substance was first noticed by Chevreuil in the soup or extract of meat, but as he obtained it in very small quantity, and other chemists did not succeed in procuring it, its composition was unknown, and its existence was even doubted, as an ingredient of flesh, Berzelius having suggested that it might be an accidental product of decomposition. Liebig showed that it is always present in all kinds of flesh, at least in all those tried by him, namely, in the flesh of the horse, ox, ox-heart, sheep, pig, calf, roe-deer, hare, marten, red-deer, fox, fowl, and pike. Schlossberger had shortly before obtained a trace of it from the flesh of an alligator, although too little for analysis, and I have since found it in the flesh of pigeon, skate, cod and haddock. Liebig observed that when the juice containing it is evaporated, the kreatine is destroyed or rendered uncrystallisable by the free acid. By neutralising, therefore, the juice, obtained as above mentioned, (after heating it so as to coagulate the albumen, and separating the coagulated albumen by filtration), with baryta water, and evaporating to the consistence of syrup at 130° or 140°, he obtained the kreatine in quantity amply sufficient to allow him to study its composition and characters. The following table contains his results and my own, in regard to the preparation of kreatine obtained from several kinds of flesh. It will be seen that in all it is small, varying from 0·607 to 3·21 per 1000.

	Liebig.	Gregory.
1000 parts of the flesh of Fowl yielded of Kreatine .	3·20	3·21 2·90
„ „ Ox-heart „ „ .	..	1·375 1·418
„ „ Cod „ „ .	..	0·935 1·710
„ „ Pigeon „ „ .	..	0·825
„ „ Horse „ „ .	0·72 .	..
„ „ Ox „ „ .	0·697	..
„ „ Skate „ „ .	..	0·607
„ „ Haddock „ „ .	..	1·504

Fowl yields the largest proportion, but kreatine is obtained much more cheaply from cod. I find that the chopped cod, well mixed with little more than its own weight of water, and pressed out, yields a fluid, which, when neutralised (after the coagulation of the albumen) by baryta, filtered to separate the phosphate of baryta, and gently evaporated till, on cooling, it forms a thin jelly, deposits, on standing, kreatine in large crystals, nearly pure. In one experiment, 25 lbs. of cod yielded 164 grains; in another, 30 lbs. yielded 356 grains. The crystals, by one recrystallisation from 6 or 7 parts of boiling water, are rendered quite pure. The kreatine obtained from haddock was less pure than that from skate or cod, and was evidently mixed with a less soluble matter, the nature of which I have not had time as yet to ascertain.

Kreatine forms brilliant hard prismatic crystals, efflorescing at 212°, very soluble in hot water, less so in cold water, sparingly soluble in alcohol. It is neutral, and its formula is $C_8 N_3 H_{11} O_6 = C_8 N_3 H_9 O_4 + 2 HO$.

By the action of acids, kreatine is resolved into the new base, kreatinine and water; and by that of bases into the new base sarcosine, and urea, as already explained.

Kreatine has been discovered, along with kreatinine, in urine. Pettenkofer obtained, by the addition of chloride of zinc to a concentrated extract of urine, a crystalline precipitate, containing chloride of zinc and an organic matter, the composition of which he found to be $C_8 N_3 H_8 O_3$. Liebig has proved that this substance is resolved by the action of alcohol into kreatine $C_8 N_3 H_{11} O_6$, and kreatinine $C_8 N_3 H_7 O_2$, and that it was in fact, as analysed by Pettenkofer, a mixture of those substances, in the proportion of 3 eqs. of the latter to 1 of the former. The original crystals of Pettenkofer were a mixture of free kreatine, with a compound of chloride of zinc with kreatinine.

The addition of chloride of zinc to the mother liquor which has deposited the kreatine from the juice of flesh, yields the compound of Pettenkofer, so that kreatinine exists ready formed in the juice of flesh.

Lactic acid. This acid, as an ingredient of the juice of flesh, is very interesting; and it is remarkable that Liebig, who demonstrated its absence in normal urine, (in which, according to Cap and Heury, it exists in combination with urea,) should have been the person who detected it in flesh. It is present in large quantity, and occurs as abundantly in the flesh of carnivorous as in that of herbivorous animals. Its origin and formation in the former is not yet explained, and is a problem of much interest. The presence of lactic acid in the juice of flesh is also important, as readily accounting for its presence in the gastric juice, which, as we have seen, is also acid. The lactic acid in the juice of flesh is obviously consumed in respiration, as will be explained hereafter.

Inosinic acid. This acid has been little studied. Its formula is $C_{10} N_2 H_6 O_{10}, HO$, and it forms, with baryta, a salt which crystallises in silvery scales.

Phosphoric acid. This acid exists in large proportion in the juice of flesh, in the form of acid tribasic phosphate of potash, $PO_5 \left\{\begin{matrix} KO \\ 2\,HO \end{matrix}\right\}$, a salt which is always produced when phosphoric acid is made to act on chloride of potassium or salts of potash. This salt is strongly acid, and chiefly contributes to the acidity of the juice. It is most important and worthy of remark, that the blood, which is separated from the juice of flesh only by the finest membranes, cell walls, or parietes of vessels, is invariably alkaline, containing the common phosphate of soda, $PO_5 \left\{\begin{matrix} 2\,NaO \\ HO \end{matrix}\right\}$, a salt which is always formed when phosphoric acid acts on chloride of sodium or salts of soda, and which is strongly alkaline.

Here we observe, first, that while soda is essential to blood, potash is equally essential to the juice of flesh; secondly, that in these two fluids, soda and potash cannot, as in so many other cases they can, replace each other; thirdly, that by this arrangement, an acid and an alkaline fluid are constantly in close vicinity to each other, separated only by membrane, at all parts of the body; fourthly, that being at the same time in contact with muscle and nerve, the conditions of electric currents are present; while such currents, as is known, have recently been proved by Matteucci to exist. Lastly, that animals cannot form blood, unless their food contain, along with phosphates, salts of soda, or at least, chloride of sodium, so that when they are fed on the land plants of certain soils, in which sodium is nearly absent, common salt must be given to them.

The function of the phosphate of magnesia, which occurs in large quantity in the juice of flesh, is not yet even conjectured; but it cannot be doubted that all the substances present, organic as well as inorganic, have each a special part to perform.

SALIVA.

The chief use of the saliva is to assist in digestion, whether by itself containing animal matter in a state of change, or by its remarkable power of inclosing and retaining bubbles of air, the oxygen of which commences the change necessary to digestion, on coming in contact with the food or the stomach and gastric juice. To serve this purpose, the saliva has a very great degree of viscidity, so that it froths up easily, and the froth does not fall readily. It is alkaline, and contains hardly more than 1 or 2 per cent. of solid matter, partly mucus, partly the usual salts, partly a peculiar soluble matter, *ptyaline.* The salts of the saliva are the chlorides of potassium, sodium, and calcium, some potash, and soda, with a large proportion of bone earth. It appears also to contain a trace of sulphocyanide of potassium: at least it reddens with persalts of iron; and although acetates do this, there is some reason to ascribe the effect here to sulphocyanides.

The *pancreatic juice* resembles saliva, but appears to be slightly acid, and contains 8 or 9 per cent. of solid matter, including ptyaline and a matter like caseine. This juice is added to the chyme in its passage through the duodenum, along with the bile and intestinal mucus.

EXCREMENTS. URINE.

The chyme, after receiving the pancreatic juice, the bile, and mucus, passes along the intestine, where the absorbents or lacteals take up the fluid part, leaving the insoluble portions. The chyle or absorbed fluid is partly conveyed into the abdominal veins, and partly made to pass through numerous glands (in which process it loses its acid reaction, becoming alkaline), from which it proceeds to the thoracic duct, and is then, with the lymph, poured into the vena cava to mix with the venous blood.

In the mean time, the insoluble parts of the chyme are rejected, and accumulate in the large intestines, various gases being disengaged, such as carbonic acid, hydrogen, carburetted hydrogen, nitrogen, and sulphuretted hydrogen.

The solid excrements of man contain very little matter soluble in water, and consist of woody fibre, with fatty, resinous, and waxy substances, and finally the insoluble salts of the food, namely, phosphates of lime and magnesia, with traces of soluble salts, and some silica.

The urine of man contains urea and uric acid, also hippuric acid, kreatine and kreatinine, and other organic compounds very imperfectly known. Its acid reaction, according to Liebig, depends on the fact that phosphate of soda dissolves uric and hippuric acids, forming an acid solution. If 40 grains of dry phosphate of soda $PO_5 \left\{ \begin{matrix} 2\,NaO \\ HO \end{matrix} \right\}$, 15 grains of uric acid, and 15 grains of hippuric acid, be dissolved in 1 lb. of hot water, a solution is formed which on cooling deposits 7½ grains of uric acid, and the remaining liquid forms an artificial urine, which, like the natural, is acid. It contains also phosphoric acid, magnesia, often ammonia, soda, phosphate of soda, common salt, sulphuric acid, or sulphate of soda, in short, the soluble salts of the food, along with sulphuric acid formed by the oxidation of the sulphur of the tissues. The addition of ammonia to urine causes a precipitate of phosphate of lime.

Fresh urine, filtered (to separate mucus) into a perfectly clean vessel, keeps unchanged for weeks or even months; but if in contact with decomposing animal matter, the urea is speedily transformed, by putrefaction, into carbonate of ammonia, while phosphate of lime is precipitated, the urine becoming strongly alkaline.

The urine of the herbivora contains much uric acid, also hippuric acid: that of the carnivora contains more urea, and is strongly acid: uric acid predominates very greatly in the urine of birds, and that of reptiles is nearly pure acid urate of ammonia.

When benzoic acid is administered internally, it appears in the urine as hippuric acid, which latter acid is generally present in small quantity in urine. The acid reaction of human urine is not owing to lactic acid, as was formerly supposed, but to free uric acid dissolved by the phosphate of soda. The urine is sometimes neutral, and always becomes alkaline, when the food contains salts of potash or soda with organic acids, because, the acids being oxidised in the body, yield carbonates of the alkalies. It is evident, therefore, that by attention to diet, the urine may be brought into any desired condition.

When water, or a very weak saline solution, is taken into the stomach in large quantities, it is rapidly absorbed by endosmosis, and the urine becomes more and more diluted, till at last it resembles the water that has been taken. But if a solution containing as much saline matter as the blood, or a little more, is taken into the stomach, it is not absorbed, and the stomach becomes so loaded that the experiment cannot be continued. If, again, the solution be much stronger, the water of the blood passes outwards by exosmosis, and produces diarrhœa. This explains the purgative action of neutral salts, which is well exemplified by sprinkling salt on a portion of fresh membrane such as bladder, or on meat, both of which yield water and are soon swimming in brine.

The salts of the urine and of the excrements, being derived directly from the food, vary according to its nature, the soluble inorganic salts of the food being found in the urine, the insoluble salts in the excrements. Thus, the ashes of the food of the carnivora contain no carbonates, but are rich in phosphates, and such also is the case with the salts (or ashes) of their excreta, liquid or solid. In fact, if we know the nature and composition of the ashes of the food, we can tell at once the salts of the urine. In an adult animal, the quantity of salts excreted is precisely equal to that contained in the ingesta, and therefore, by altering the food we can alter at pleasure the nature of the salts in the urine.

As an example, we may here adduce the case of the horse, which animal consumes, in his food, a certain quantity of mineral substances, derived ultimately from the soil :—

THE HORSE

Consumes of Mineral Substances,			Excretes of Mineral Substances,		
	oz.			oz.	
In 15 lbs. of hay,	18·61	21·49	In the urine .	3·51	21·87
In 4·54 lbs. of oats,	2·46		In the fæces .	18·36	
In water . .	0·42				

The above result is one obtained by actual and very careful experiment, and the nature of the salts is found to be the same, as indeed must obviously be the case, as long as the animal does not change its weight. A growing animal will retain the phosphates in part to aid in forming bone, and an old or wasting animal will give out more salts than are taken in.

It is obvious that analyses of urine or excrement are unnecessary if we can examine the food; and that in general they must be useless, since we can never expect the same result twice, unless where the food is not varied.

The excrements, according to Liebig, represent the incombustible and unburned, or partially burned ingredients of the food, and, if we view the body as a furnace, in which the animal heat is produced by the oxidation or combustion of the food, they correspond to the soot and ashes of a common fire. That they contain partially oxidised matter is proved by the fact, recently observed by Liebig, that the albuminous compounds, when partially oxidised by fusion with potash, yield, on the subsequent addition of an acid, volatile matters possessing, according to the albuminous substance employed, the peculiar odours which characterise the fæces.

Guano, so highly prized as a manure, is the decayed excrement of sea fowls, which was originally, like that of reptiles, and indeed also of birds in general, mixed urine and fæces, the urine being solid or semisolid, and consisting of urate of ammonia. It varies much in the proportions of its ingredients, both because the original excrement must have varied according to the food of the birds in different places, and also because some specimens have not been so long exposed to air and moisture as others, and some are almost fresh. Thus some guano contains upwards of 30 per cent. of uric acid, while in other specimens hardly a trace of that acid is left. The better qualities of guano contain much ammonia, partly free or as carbonate, as proved by its odour, partly combined, as sal ammoniac, oxalate, urate, and phosphate of ammonia, and magnesia. They also contain phosphate of soda and much phosphate of lime, the latter being derived from the bones of the fish on which the birds fed. There are also found sulphate of potash and soda, and oxalate of lime, in guano. The remainder is water, and a brown matter like humus.

It is easy to see that guano must act chiefly as a source of ammonia and of earthy and alkaline phosphates, so valuable to growing plants, especially to those cultivated for food; and that its value depends very much on the amount of phosphates it contains. But while the value of guano is unquestionable, let us not overlook the fact, that while we are ransacking the most remote islands for guano, that substance supplies us with nothing but the mineral salts and the ammonia which have formed crops of vegetables and races of animals at some former period, and that it differs in no essential point from the fresh or modern excreta of man and animals nearer home, which excreta, at least those of man, the most valuable of all, we allow to be carried into the sea in quantities which may be measured by the food we consume. In fact we take out of the sea, in the shape of guano, only part of what we throw into it in the contents of our common sewers. These valuable matters, instead of being carefully collected and preserved, as in China, are sent to form the food of sea plants: on these plants animals feed, which animals serve as food to fish. The fish are consumed by sea fowl, and we recover in their excrement a part of what we are constantly throwing away. Another part of what we lose we recover in this country, at a great expense, in the shape of bone-earth, which, however, must be taken from other countries. We shall return to this subject: meanwhile, let us express a hope that Europe will at length follow generally, as in some districts it has done, the rational example set by the eminently practical Chinese, of restoring to the soil, as nearly as possible, in the shape of excreta, what we take from it in our crops and cattle, and thus keeping up its fertility.

URINARY CALCULI.

These are of various kinds, according to the peculiar condition of the urine.

Uric acid calculus is the most frequent, being the usual deposit when the urine is acid. Its origin, as a calculus or deposit, that is, in abnormal quantity, is owing to deficient aeration, much oxygen being required to resolve it into soluble compounds, such as urea, carbonate of ammonia, or even oxalic acid. Hence sedentary habits, highly carbonised food, and indulgence in strong wine, all favour its production: the first by diminishing the supply of oxygen, the two latter causes by seizing on the oxygen to the exclusion of the uric acid. It is easily recognised by the action of potash, which dissolves it, and forms a solution from which acids precipitate uric acid: or by nitric acid, which dissolves it with effervescence, and yields, on evaporation of the solution, a deep red stain, becoming purple with potash. Uric acid calculus is commonly tinged more or less red or brown. When pure it is entirely dissipated before the blowpipe.

Urate of ammonia also occurs, and is distinguished from uric acid by disengaging ammonia when dissolved in potash.

Phosphate of lime is very frequent when the urine is neutral or alkaline. It is white and earthy, soluble in nitric acid, and precipitated by ammonia. It is fixed in the fire.

Phosphate of ammonia and magnesia is also pretty frequent. It dissolves easily in acetic acid, and when heated gives off ammonia, leaving a solid mass soluble in acids.

Fusible calculus is a mixture of the two preceding. It melts readily before the blowpipe.

Oxalate of lime constitutes the mulberry calculus, and often appears as minute crystals in the urine. When heated, it leaves carbonate of lime; or if heated in a tube with oil of vitriol, it gives off carbonic oxide. It dissolves in acids, and is precipitated by alkalies.

Carbonate of lime occasionally, but very rarely, constitutes a urinary calculus, easily recognised by the action of hydrochloric acid, which dissolves it with effervescence, and by a red heat, which leaves quicklime.

Cystic oxide or *cystine*, and *xanthic oxide*, are very rare calculi. Their characters and composition have been given under *Uric Acid.*

LYMPH.

This fluid may be looked on as blood devoid of its colouring matter. When drawn from the vessels, it coagulates like blood, from the separation of fibrine; and the liquid in which the coagulum has formed itself, coagulates, when heated, like the serum of the blood. Human lymph contains about 96 per cent. of water, and variable proportions of albumen, fibrine, and salts, the salts amounting to nearly 2 per cent.

BLOOD.

This important fluid, from which the whole animal body is formed, and by which it is supplied and nourished, is a thick, somewhat viscid, alkaline liquid, of a slight saline taste, and a peculiar faint odour. It is deep red and opaque, and has a density of 1·0527 to 1·057.

It is made up of an immense number of *globules* or flattened disks, floating in a limpid yellowish fluid. When drawn, it soon coagulates, forming a trembling jelly, which gradually contracts, expressing a yellowish liquid, *the serum*, which is occasionally turbid, and is always alkaline to test paper, and saline to the taste.

The coagulation consists in the separation of the fibrine previously dissolved, which, owing to some unknown cause, assumes the insoluble state, forming a fine network or jelly, in which the globules are inclosed. If the blood be beaten with a rod, the fibrine separates perfectly and adheres to the rod; but it is in the form of white filaments, and the globules remain suspended in the serum, no jelly whatever being formed in this case. Or if the fresh blood be mixed with 8 times its bulk of solution of sulphate of soda, no coagulum is formed, the fibrine remains dissolved, and a sediment is deposited which contains the globules unaltered.

The *red globules* thus prepared may be collected in a filter. Pure water added to them, or to the coagulum of blood, rapidly alters their form, and in fact dissolves them into an opaque liquid. This action of water is thus explained: the globules are formed of a thin, colourless, and transparent coat, inclosing a very soluble colouring matter. They float in a saline liquid, in which there is equilibrium between the contents of the globules and the fluid surrounding them. But when the latter is diluted with water, the equilibrium is disturbed, and endosmosis takes place, by which the contents of the globules acquire so greatly increased a volume, that the globules burst and their contents are dissolved in the water. The torn membranes of the globules may be detected by the microscope.

In saline solutions, the globules do not absorb water any more than in the serum. When collected in a filter, the globules form a red mass of the consistence of honey, consisting of fibrine and albumen, the latter in combination with the colouring matter. In a concentrated solution of chloride of calcium, the globules lose water by exosmosis, and contract in volume. If now placed in pure water, the globules again swell, and burst, forming a jelly which dissolves in water. The solution, on standing, deposits fibrine in white membranous masses, and the supernatant liquid, when boiled, is coagulated, indicating the presence of albumen.

The *colouring matter* of the blood is contained in the globules in combination with albumen, but is unknown in a state of purity. The compound of albumen and colouring matter is of a deep-red colour, becoming bright in contact with air or oxygen, and being rendered nearly black by carbonic and sulphurous acids, sulphuretted hydrogen and sulphurets. Protoxide of nitrogen gives it a purple colour.

The red compound gives 2 per cent. of ashes, of which $\frac{1}{3}$ is peroxide of iron; and iron is uniformly present in red blood, which is the only animal product in which it occurs. This iron cannot be detected in the globules or their contents by the usual tests, but after passing chlorine through the red solution till the colour is destroyed, the iron may be detected by ferrocyanide of potassium.

When the red compound of albumen and colouring matter above mentioned is moistened with oil of vitriol, so gradually as not to become warm, a pasty mass is obtained, which attracts moisture from the air and forms a red jelly. If this be very gradually rubbed up with pure water, it contracts into a dark-red matter, which is surrounded with a colourless or yellowish liquid. This liquid is found to contain all the iron, and the dark matter, when calcined, leaves a white ash entirely free from iron, if the operation has been well performed. I have repeated this interesting experiment, first devised, I believe, by Sanson, which proves that, although the red compound contains iron, yet the colour does not necessarily depend on that metal; for the colour is altogether uninjured by the complete removal of the iron just described, although the colouring matter actually obtained in this experiment is not the original colouring matter of the blood, but modified.

The *Hematosine* of Lecanu is also a product of decomposition. It is prepared by means of diluted sulphuric acid, alcohol, and ammonia, by a tedious process. It is dark-brown, and forms red solutions with the alkalies, being insoluble in water, alcohol, and ether. It contains part of the iron of the blood, but as some kinds of hematosine contain $\frac{1}{4}$ or $\frac{1}{3}$ more iron than others, while its properties continue the same, it is obvious that the iron does not contribute essentially to those properties, such as the colour. Hematosine contains 6 to 8 per cent of iron.

But the iron serves an important purpose in the blood; and we have reason to think that it is present in the form of oxide, for sulphuretted hydrogen and soluble sulphurets cause the blood to become first green and then black, owing to the formation of sulphuret of iron—a character indicating either the oxide or some corresponding compound, and not a compound like ferrocyanogen, in which the sulphurets cannot detect the iron. Moreover, we see that oil of vitriol dissolves out oxide of iron; and although alkalies and ferrocyanide of potassium do not detect it, this is owing to the blood being an alkaline liquid, and to the presence of so much animal matter.

It is from the blood that are formed the tissues, the cells, muscular fibre, nervous matter, &c., &c.; and we may, therefore, expect to find some relation between their composition and that of the blood. In fact, flesh, or muscular fibre, as it exists in the body, including vessels, nerves, fat, &c., has exactly the same composition as the blood has on an average of venous and arterial, or a mixture of both. We may, therefore, look on muscular fibre, or animal flesh, as simply blood more highly organised.

In addition to the substances mentioned above, namely, albumen, fibrine, colouring matter, and salts, blood also contains fat, apparently cholesterine, along with fatty acids and a peculiar fat, called *seroline*.

The normal proportions of serum and clot are 87 per cent. of serum to 13 of clot. 1000 parts of human blood contain 869·15 of serum, of which 790·37 are water, 67·8 albumen, and 10·98 are salts and fatty matter: along with 130·85 of clot, containing 125·63 albumen and fibrine of the globules, and 2·27 hematosine (a little fatty matter and traces of salts being present in all three), also 2·95 of fibrine, separate from the globules.

Venous blood contains more water and fewer globules than arterial blood.

The blood contains gases, chiefly carbonic acid and nitrogen, which it gives off in vacuo, or in a current of hydrogen. It is said to contain free oxygen, but this seems very improbable, when we reflect that fibrine absorbs oxygen, transforming it into carbonic acid, and that blood is instantly altered by contact with oxygen. The change from venous to arterial blood, from dark to florid, depends on the presence of oxygen, but also requires the presence of a saline solution. Indeed, a similar change of colour takes place in vacuo if the clot of venous blood be there covered with a pretty strong solution of various salts.

One chief function of the blood is, after conveying oxygen to all parts of the system, to carry to the lungs, there to be exhaled, the carbonic acid formed in the extreme vessels. For this purpose it is admirably adapted, from the fact that it is alkaline, and that its alkalinity depends on the phosphate of soda, $PO_5 \left\{\begin{matrix} 2\,NaO \\ HO \end{matrix}\right\}$, a salt, the solution of which absorbs carbonic acid better than a solution of carbonate, and, when in contact with air or oxygen, gives off *the whole of it*, whereas a carbonate, if it absorbed as much, would give up only half of the quantity absorbed. This important property of phosphate of soda has recently been demonstrated by Liebig; and we can now see why potash cannot replace soda in the blood, since the tendency of potash is to form an acid phosphate, $PO_5 \left\{\begin{matrix} KO \\ 2\,HO \end{matrix}\right\}$. Liebig and Enderlin have also proved that the blood does not, as had been asserted, contain carbonate of soda.

THE NUTRITION OF PLANTS AND ANIMALS.

The animal and vegetable kingdoms of nature are connected together in a beautiful system of mutual dependence, exhibiting a perpetual circulation of certain elements through both, the mineral kingdom being the point of departure and that also where the circulation terminates, to recommence unceasingly.

Plants derive their nourishment exclusively from the mineral world. It is clear that the first plants must have done so; and although the decaying remains of former plants now contribute to vegetation, we shall see that they do so under mineral forms, and not essentially: they promote vegetation, but are not indispensable to it.

The mineral food of plants, then, consists of carbonic acid, water, and ammonia, all of which are obtained from the atmosphere, and of sulphur (sulphuric acid), phosphorus (phosphoric acid), alkalies, earths, salts, and metals, all derived from the soil. Without the aid of the matters derived from the soil, the most abundant supply of carbonic acid, water, and ammonia, is of no use. But if a soil contain these necessary substances, plants will thrive in it, even if they have no carbonic acid or ammonia furnished in the shape of manure beyond the usual atmospheric supply.

During germination, oxygen is absorbed and carbonic acid produced: starch is transformed, probably by the action of diastase, or of an acid developed during germination, into sugar or dextrine, which being soluble, are fitted for being conveyed to all parts of the plant. Meanwhile the azoto-sulphurised ingredients of the seed also become soluble, and with the sugar, &c. contribute to the formation of new parts destined to collect food from the air or the soil.

The leaves and roots, as soon as formed, absorb carbonic acid from the air and from the soil. Alkalies are at the same time taken up by the roots, and with their aid the carbonic acid, under the influence of light, is decomposed, its carbon being retained, while its oxygen is given off. At the same time, water, ammonia, sulphuric acid (or a sulphate), and phosphoric acid or phosphates are taken up, and their elements, along with the carbon, give rise to fibrine, albumen, caseine, &c.

It is probable that the fixation of carbon is a gradual process, having successive stages; that the carbonic acid is first reduced or deoxidised so far as to yield oxalic acid; thus $C_2O_4 - O = C_2O_3$; that oxalic acid, with the aid of water, is farther reduced, so as to yield malic or citric or tartaric acid; thus, $C_4O_6 + 2HO = C_4H_2O_8$; and $C_4H_2O_8 - O_4 = C_4H_2O_4$; this last formula doubled is that of anhydrous malic acid, $C_8H_4O_8$. From this and similar compounds, sugar, $C_{12}H_{12}O_{12}$, starch, $C_{12}H_{10}O_{10}$, gum, $C_{12}H_{10}O_{10}$, and woody fibre, $C_{12}H_9O_9$ or $C_{36}H_{22}O_{22}$, are easily deduced, by the addition of the elements of water and the elimination of oxygen. Thus, 3 eq. hydrated malic acid, $C_{24}H_{18}O_{30}$, plus 6 HO and minus O_{12}, is equal to 2 eq. dry sugar of grapes, $C_{24}H_{24}O_{24}$. There is good reason to think that the chief function of the alkalies in plants is to promote these metamorphoses.

Water not only acts by its elements, but also as the indispensable solvent through which the whole food of plants, especially that derived from the soil, can alone enter them.

From the above considerations we may draw several useful inferences.

1. The presence of decaying vegetable matter in the soil promotes vegetation by furnishing a steady supply of carbonic acid gas. The proportion of decaying matter or humus must not exceed a certain limit; otherwise there is too much carbonic acid in the air of the soil, and the plant dies in such circumstances.

2. The presence of decaying azoto-sulphurised matter in the soil is very advantageous, furnishing a supply of ammonia, which is essential to vegetation, and is scantily supplied by the atmosphere.

3. The supply of carbonic acid and of ammonia can only favour the development of vegetation in so far as alkalies, silica, phosphates, and sulphates are supplied by the soil.

4. Since all the azoto-sulphurised principles, albumen, fibrine, caseine, &c., contain sulphur and phosphorus, or rather phosphates, it is evident that seeds and such other parts of plants as contain these principles can only be developed in so far as the soil contains alkaline or earthy phosphates and sulphuric acid or sulphates.

5. If the soil be rich in alkalies, sulphates, and phosphates, and if it also contain soluble silicates, essential to the stem of the grasses and cerealia, it is fertile for all nutritious crops; and such crops will, in that case, derive from the atmosphere alone all the carbon and nitrogen (carbonic acid and ammonia) they require, *provided time be allowed.* The advantage of decaying organic matter, or of manures containing ammonia, in such a soil, consists in shortening the time necessary for the development of the plant; a matter of the last importance in our uncertain climate, but of far less consequence in southern regions, where summer is perhaps twice as long.

6. The ashes of wood, straw, leaves, &c., consisting entirely of matter extracted from the soil by the plants for the purposes of vegetation, must prove a most fertilising manure: and in all cases the ashes of any crop must be the best manure for that vegetable.

7. But as the ashes of plants are represented by the excreta of the animals (or the ashes of these excreta) which fed on them, so the excreta of animals fed on turnips, hay, straw, potatoes, &c., must be the best manure for turnips, hay, corn, and potatoes respectively.

8. When by the addition, to an average soil, of guano, or of bone earth, a very heavy crop is obtained, say of wheat, we are not to expect that a repetition of the same treatment will produce the same effect. We must bear in mind, that the presence of the increased supply of phosphates has enabled the plant to take up a much larger quantity than otherwise it could have done, of alkalies, silicates, and the other necessary minerals. Since we have not added those substances in our guano or bone earth, it may happen that the soil is exhausted of its whole actually available supply of them by that one crop, and that years may elapse before it becomes, in the course of nature, as fertile as before.

9. The only certain rule is this : as far as possible to restore to the soil, in the shape of manure, exactly what it has lost in the crop ; if the soil were originally fertile this will maintain its fertility, which will even be gradually augmented by the action of the weather on the soil and subsoil.

10. With a view to this, every particle of solid or liquid manure, especially human, should be preserved with the utmost care. It is their mineral elements which are the most valuable ; and since these have all come from the soil, in preserving them for manure we are only restoring what we have taken away. This has long been systematically done in China, and is also generally practised in the Netherlands ; but in this country the waste of valuable manure is lamentable, and is necessarily followed by a slow but certain deterioration of our soil and crops, which we are now endeavouring to remedy by the expensive, precarious, and partial measure of importing bone earth and guano. But guano will, ere long, be exhausted ; and when other countries know the real value of their bone earth, they will not willingly part with it, at all events not except at a very high price.

11. If a soil is not fertile generally, it must be deficient in most of the substances above alluded to ; but if it yields good crops of one vegetable and not of others, it must be wanting in the characteristic mineral elements of the latter, which must then be supplied.

12. The ashes of plants being known, the fact that a certain vegetable, cultivated or wild, thrives in any given spot, furnishes us with an analysis of the available or soluble elements of the soil, and enables us to direct our measures of improvement according to the crop we wish to raise.

Although certain bases characterise the ashes of certain plants, as potash does those of turnips and potatoes, and lime those of peas, beans, &c. ; yet in many cases, one base may be substituted for another, as soda for potash, or magnesia for lime.

It is maintained by some that carbon is introduced into plants, in part, as humus, humic acid, or humate of ammonia, dissolved in the juice, and derived from the mould in the soil. But there is no evidence that fertile soils contain humus in a form soluble in water, and the sap, when first entering the plant, is colourless, while all solutions of humus, &c., are brown. Besides, in forest land, which is not manured, the proportion of humus or of carbon in the soil, instead of diminishing, rather increases, while enormous quantities of carbon are removed annually in the shape of wood. Here, as in the case of the first vegetables, it is plain that all the increase of carbon must be derived from carbonic acid : since, if the plant does absorb humus or humic acid, or humate of ammonia, which there is no proof that it does, it must give to the soil as much or more humus, &c., as an excretion from its roots.

It has also been argued by some that plants may obtain their nitrogen, either directly by absorption of the nitrogen of the atmosphere, or by causing that gas to form ammonia, combining with hydrogen derived probably from water, &c. ; or, lastly, from the decomposition of nitric acid, which acid is supposed to be formed in the atmosphere by direct combination of its elements. But no evidence has ever been given, either that plants can absorb nitrogen directly, or that they can cause the nitrogen of the atmosphere to combine with hydrogen. As for nitric acid, although traces of it have been observed in thunder-storms, it does not appear to be formed in sufficiently large quantity ;* and if it were, no proof has yet been offered that plants can derive their nitrogen from it. The action of nitrate of potash, or of soda, as manure, proves nothing, because it may be due to the alkalies alone, and probably is so, since they do not seem to act better than other salts of the same bases. Moreover, many plants, such as tobacco, and sunflower, contain much nitrate in their juices, and therefore appear rather to form nitric acid than to destroy it. On the whole, it appears nearly certain that ammonia is the only source of nitrogen in plants. It is self-evident that the atmosphere must contain ammonia, derived from the putrefaction of animal and vegetable matter, and also that, however small the *proportion*, the absolute quantity in the air at any one time must be sufficient for the supply of the vegetable world, and through it of the animal world, since all animals and vegetables ultimately putrefy, giving off their nitrogen in the form of ammonia. It is quite easy to detect ammonia in rain-water, by which means it is conveyed to the roots or leaves of plants; and it has also been proved that the juices of plants contain abundance of ammonia.

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* In fact, the proportion of nitric acid thus formed, is so very small as to lead to the conclusion that it is formed only from the ammonia present in the atmosphere. Should this prove true, as is highly probable, then ammonia will be the source of all the nitrogen of plants, even if part of that nitrogen should be derived from nitric acid. It is generally admitted that in nitrification the whole of the nitric acid is derived from the oxidation of ammonia.

The nutritious principles, albumen, fibrine, and caseine, are formed by plants alone from ammonia, sugar (or gum, starch, &c.), sulphates, and phosphates. They pass into the body of animals, and are there converted into blood. As they cannot be formed nor exist without the phosphates, so by their means the animal body is supplied with bone earth, and with the soluble phosphates necessary for the other tissues.

In the animal body, the leading and characteristic action is the absorption of oxygen and the oxidation of the tissues: that is, of carbon and hydrogen, so that animals take up oxygen, and give out carbonic acid. This is the reverse of what occurs in plants, which absorb carbonic acid, and give out oxygen.

In the lungs, oxygen enters the blood, and is carried, apparently, by the agency of a compound of iron, to every part of the body. The oxidation of the effete, or worn-out tissues, which have meanwhile been replaced by the blood, takes place in the capillaries, and is, in all probability, the source of the animal heat. The final result of this oxidation is the production of a large quantity of carbonic acid and water, which are given off by the lungs and skin.

Health, in the animal body, consists in the due balance or equilibrium between the oxidising, or destructive agency of the atmosphere, and the process of nutrition by which the other is compensated.

Since the nutritious, or blood-forming elements of food, have the same composition as the albumen, fibrine, &c., of the tissues —indeed, in the case of animal food, are identical with them— we may consider the process of oxidation and destruction, either as affecting the food directly, or, what is more probable, those portions of the tissues which, having performed their functions, are to be thrown off. But we must not forget that in the herbivora, a great part of the combustion which yields the animal heat is carried on at the expense of those parts of the food which cannot form blood: namely, sugar, starch, or gum, fat, &c.

The fat of the animal body is, at all events in great part, derived from the non-azotised elements of the food when these are in excess, and oxygen is deficient. In these circumstances, the deficiency of oxygen is supplied at the expense of sugar, starch, or gum, which by losing oxygen, gives rise to fat; for the proportions of carbon and hydrogen in sugar, &c., and in fat, are exactly the same, that of oxygen alone being different. Hence the conditions favourable to the formation of fat, are abundant farinaceous food, and rest, that is, defective aeration, as is seen in stall-fed animals, and in the fattening of geese fed on maize and deprived of the power of locomotion. The formation of wax, a species of fat, from sugar by the bee, is another example.

The greater part of the effete nitrogen is given off in the form of urea; while the carbon, with part of the nitrogen, the sulphur, and the soda, take the form of bile. The bile undergoes resorption in the intestines, and is oxidised or burned, yielding, as an intermediate product, lactic acid, which we find playing an important part in the gastric juice and the juice of flesh, but of which no trace reaches the kidneys. The combustion of the bile is one chief source of the animal heat.

The phosphates of the food, being brought in contact with salts of potassium and sodium, yield with the former the acid phosphate of potash, characteristic of the juice of flesh and the gastric juice, and, with the latter, the alkaline phosphate of soda, which gives its character to the blood, and conveys the carbonic acid to the lungs.

As was formerly hinted, the acid juice of flesh and the alkaline blood, separated by membrane, and in contact with nerve and muscle, appear to produce electric currents, the importance of which cannot as yet be fully appreciated, but the existence of which is certain.

The food of animals may thus be said to be literally burned in their bodies, and this, as in the case of other combustibles, for the purpose of producing heat. The gaseous products of the combustion are sent off through the skin and lungs, while the smoke, soot, and ashes are represented by the excrements and urine.

The food required by animals must bear a certain relation to the waste of matter, and to the heat required. Thus, a hard-working man, in whom the change of matter is rapid, requires much more food (blood, or proteine compounds) than a sedentary person; and in cold climates a much larger quantity of food rich in carbon, especially fat, blubber, and similar matters, is necessary than in warm climates, where, indeed, such food excites invincible repugnance. Any misproportion in the amount or nature of the food has a tendency to induce disease. Thus, Europeans, who often eat and drink as at home when they go to tropical countries, pay the penalty of their ignorance in the very frequent liver complaints observed among them. For the same reason, hepatic disease is more frequent during summer than during winter.

After death, the animal body is slowly, but surely, resolved into the ultimate products of putrefaction, namely, carbonic acid, water, and ammonia, which rise into the atmosphere, having completed the circuit through which we have traced them, in order to recommence it by once more contributing to the growth of plants on which animals will again feed.

The bones of dead animals are also by degrees restored to the soil from which they are taken; and nothing is finally lost. Even the rich manure which we recklessly cast into the sea, serves as nourishment for sea plants, on which are fed fish, which, in their turn, become food for sea fowl, the excrements of these last, in the shape of guano, returning to fertilise the fields from which their mineral elements were perhaps originally taken.

It is evident that there must be a balance or equilibrium kept up between the animal and vegetable worlds. For the atmosphere in which both live does not, at least perceptibly, change in its composition. There is no appearance either of increase or dimunition, in the proportion of oxygen, or in that of carbonic acid. Yet we know that animal life tends directly and powerfully to increase the proportion of carbonic acid, and to diminish that of oxygen, while the tendency of vegetable life is exactly the reverse. Hence, if in any quarter, population or animal life extends, a corresponding augmentation of vegetable life must somewhere be the result; or if, by cultivation, the amount of vegetation in any quarter is increased, the inevitable consequence must be an extension of animal life, otherwise the air would become richer in oxygen. As both carbonic acid and ammonia are partly supplied to the atmosphere from the earth itself, not merely from the decay of organic matter at the surface, but from great depths, as for example in hot springs, so we may conceive the absolute amount of carbonic acid and ammonia on the surface of the earth and in the atmosphere to be somewhat greater now than some thousand years ago. If not, then the increase of animal and vegetable life in one part of the globe must necessarily cause a diminution of one or both in some other part, since, at all events, the atmosphere becomes neither richer nor poorer in carbonic acid and ammonia. Should an addition of these substances be made, they would instantly be appropriated by the vegetable kingdom, and converted into food for animals, of which an additional number would soon be produced by the increased supply of food; and thus the aggregate amount of animal and vegetable life might be increased, while the composition of the atmosphere remained unchanged, the vegetable world exactly balancing the animal, because each produces the food of the other, as the necessary result of its own existence.

Such is a very brief and general sketch of the chemistry of animal and vegetable life, as far as we are at all acquainted with it. It is only within a very short time that this department of science has been properly cultivated, but the results already obtained are most important and highly encouraging. When we reflect that the processes by which carbonic acid, water, ammonia, and the salts of the soil are made to assume the forms, first of vegetable and then of animal tissues, as well as those by which these tissues are again resolved into the elements of which they were formed, are, and must be, purely chemical processes of combination and decomposition, governed by the laws of chemistry as ascertained by observation and experiment, but modified by the vital force, it is easy to see that from the assiduous study of the chemical changes going on in plants and animals, in health and in disease, we may confidently expect the most beneficial results. All that has hitherto been done has only pointed out the path to be followed in order to obtain valuable and permanent results. But enough has been gained to satisfy all who are acquainted with the actual state of physiology, that henceforth, it is chiefly to chemistry that we must look for the extension and improvement of physiological science. We see, for example, from the facts recently ascertained in regard to the phosphates of potash and of soda in the juice of flesh and in blood, that it is necessary to study the most minute and apparently insignificant properties of such acids and bases as occur in the organic world; since the difference in the relations of these two alkalies to phosphoric acid, long since pointed out by Graham in his admirable researches on the phosphates, and looked upon as a matter merely of scientific curiosity, has lately been shown to be the foundation of the distinctive properties of the two important fluids just mentioned. The same remark applies to the relation of phosphate of soda to carbonic acid; and this lesson is the more impressive, from the fact that potash and soda, which in these instances differ so widely, in many other cases replace each other without material change of properties in the compound. It is not, therefore, surprising, that already a knowledge of chemistry is admitted to be indispensable to the physiologist; and before long this opinion will be so far acted on that no one who is not well versed in chemistry will venture to write on physiological subjects.

ADDENDUM.

To page 182.

d. Ferric Acid, $FeO_3 = 52{\cdot}039$. Recent researches have established the existence of this compound, which corresponds to Manganic Acid. It is very easily decomposed, and is hardly known in a separate state. Ferrate of potash may be obtained in solution by igniting oxide of iron with nitre, or by passing chlorine through aqua potassa in which peroxide of iron is suspended. The solution has a very fine and intense purple colour, which, however, is not very permanent.

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